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NaCl(001) surfaces nanostructured by Suzuki precipitates: a scanning force microscopy study

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\textbf{Abstract.} Suzuki precipitates on the (001) surfaces of as-cleaved and additionally annealed NaCl:Cd\textsuperscript{2+} crystals were studied by means of dynamic scanning force microscopy and Kelvin probe force microscopy in ultra-high vacuum. Rectangular precipitates with edge lengths of up to several hundred nanometres can be found on the surfaces of as-cleaved crystals. The precipitates exhibit steps, which are a result of the cleavage of dislocations at the Suzuki–NaCl interfaces. Additional annealing of the crystals below 260 °C leads to surface diffusion and to a restructuring of the whole surface producing atomically flat precipitates at steps, but also on flat terraces in regions of low step density. On surfaces evaporated at 350 °C, the main surface characteristics of evaporated (001) surfaces of pure NaCl can be found. The step edges are merely changed in shape by nanometre-size Suzuki precipitates.

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1. Introduction

Recently, Suzuki precipitates on (001) surfaces of Mg\(^{2+}\)-doped NaCl crystals were characterized at the atomic scale by means of dynamic scanning force microscopy (dynamic SFM) and Kelvin probe force microscopy (KPFM) [1]. These nanostructured (001) surfaces exhibit two types of surface regions, which can be potential templates for nano-objects like metal nanoclusters or molecules. Because of their insulating character, the surfaces of alkali halide crystals are currently of high interest in nanotechnology [2]–[9].

The main characteristics of the Suzuki phase are its cubic structure being almost twice as large as that of NaCl, the high concentration of ordered cation vacancies and the embedding of Suzuki precipitates in the NaCl matrix [10]. The composition is given by Na\(_6\)MCl\(_8\) (6NaCl × MCl\(_2\)), where the NaCl lattice serves as a host for divalent metal impurity cations (M\(^{2+}\)) and sodium vacancies (V) occupying alternately the sodium corners of the original NaCl unit cell. The precipitates decorate steps and appear also on the flat terraces in regions of low step density [1].

For studying the topography and structure of such precipitates on the surface and in the bulk of alkali halides, electron microscopy techniques were used between the late 1960s and early 1980s and revealed already many interesting and important phenomena [11]–[21]. However, SFM allows imaging the complete topography including the height of objects on surfaces as has been shown before on the (001) surfaces of pure alkali halide crystals [22, 23]. Furthermore, SFM in its dynamic mode allows true atomic resolution imaging [24], which can be successfully applied on the (001) surfaces of alkali halides [25]–[27] even in the presence of defects [1, 28]. Additionally, the Kelvin modulation technique can be implemented, which yields useful information about the surface charge distribution on insulator surfaces [28]–[30]. Due to the latter advantages, a detailed dynamic SFM and KPFM investigation of Suzuki precipitates is desirable.

In this paper, a detailed description of Suzuki precipitates on the (001) surfaces of alkali halides is given, and dynamic SFM in combination with KPFM measurements are presented. Emphasis is given on the differences in the appearance of Suzuki precipitates, which can be found on the surface directly after ultra-high vacuum (UHV) cleavage of a crystal and after

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2. The Suzuki structure

The Suzuki phase was first introduced by Kazuo Suzuki for NaCl in 1961 [10], whereas other quite similar structures were already discussed for MgO:Mn$^{4+}$ and CuO:Pb$^{4+}$ in the 1950s [31, 32]. The phase was studied mainly in the 1970s and 1980s and has been the subject of only a few papers in recent years. Because the Suzuki phase is not commonly known today and because a detailed knowledge of its atomic structure is of importance for the observations discussed in this paper, the main properties of the Suzuki phase are presented in the following with the help of figure 1.

If the four sodium corner ions (Na$^+$) of the NaCl unit cell (figure 1(a)) are alternately exchanged with two metal impurity ions (M$^{2+}$) and with two Na$^+$ vacancies (V), an eighth of the Suzuki unit cell is formed (figure 1(b)). An enlargement of the latter cell as shown in figure 1(c) yields the unit cell of the Suzuki phase. The Suzuki unit cell is almost two times larger than the NaCl unit cell ($a_{\text{Suzuki}} \approx 2a_{\text{NaCl}}$ [36]) and includes a high density of M$^{2+}$ impurity ions and additional annealing of a cleaved crystal in UHV. The latter reconstructs the surface by diffusion and evaporation processes. The present work gives an overview of the three different types of surfaces (as-cleaved surface, surface restructured by diffusion and evaporation) and comments on how the surface is nanostructured. Alongside new findings, a comparison with previous experimental results and a discussion about defects like steps and dislocations at the atomic scale are included. Dynamic SFM measurements of cadmium-doped sodium chloride crystals are presented for the first time.
Na+ vacancies, which are highly ordered in the atomic structure of the Suzuki phase. Along equivalent (100) directions, the Suzuki cell is built by alternating layers of pure NaCl and layers that include the M2+ impurity ions and Na+ vacancies. Hence, a (001) surface can be principally terminated by a layer of pure NaCl (e.g. layers 2 and 4 in figure 1(c)), which is called, in the following, the NaCl-terminated Suzuki surface, or a defect rich NaCl layer including the Na+ vacancies and M2+ ions (layers 1, 3 and 5 in figure 1(c)). The latter type of surface is called the Suzuki-terminated Suzuki surface. The atomic structure of both types of (001) surface is shown in figure 1(d) and (e). The first layer of the NaCl-terminated Suzuki surface is a ‘normal’ NaCl layer, which can be found in pure NaCl. Both types of ions (Na+ and Cl−) form a sublattice along equivalent (110) directions with a size of $a_{Na} = a_{Cl} = a_{NaCl}/\sqrt{2}$. However, in view of the second layer below (see figure 1(e)) the NaCl-terminated Suzuki surface is not comparable to the normal (001) surface of NaCl: below the Cl− ions, either an Na+ ion, an Na+ vacancy or an M2+ ion can be found, which have considerably different bondings to the Cl− ions. However, as shown in another work [33], only the Cl− ions above the Na+ vacancies relax about 40 pm out of the surface. The other ions in the layer do not relax much from their ideal NaCl positions.

The Suzuki-terminated Suzuki surface includes the Na+ vacancies (V) and M2+ ions, which each form the largest possible sublattice with a size of $a_{V} = a_{M} = a_{Suzuki}/\sqrt{2}$. The sublattice is rotated by 45° with respect to the Suzuki unit cell and is oriented along equivalent (110) directions. The next smaller sublattice is the one formed by the Na+ ions, which is parallel to the Suzuki unit cell with half its size ($a_{Na,S} = 1/2a_{Suzuki}$). The smallest sublattice is the one formed by the Cl− ions, which is again rotated by 45° with respect to the Suzuki unit cell and which has a size of $a_{Cl} = a_{Suzuki}/2\sqrt{2}$. Thanks to the specific geometry of the Suzuki-terminated Suzuki surface, all ions and the vacancies can be unambiguously identified in dynamic SFM images with atomic resolution [1, 33].

Most of the relevant literature deals with the Suzuki phase in NaCl: Cd2+ crystals [10, 12, 14], [19]–[21], [34]–[44]. However, also other metal impurity cations such as Mn2+ [13, 14], [16]–[19], [36], [40]–[42], [45]–[50], Mg2+ [1, 21, 36, 41, 42], Fe2+ [15, 17, 19, 36, 41, 42, 51], Ni2+ [42, 52], Co2+ [53], Sr2+ [42, 54] and Pb2+ [42, 55] have been the subject of many investigations and discussions. In fact, the host lattice need not necessarily be NaCl: the Suzuki phase may exist also in NaBr (Mn2+ [50]), KCl (Sm2+ [57], Pb2+ [58] and Eu2+ [56, 59]), KBr (Mn2+ [60] and Eu2+ [59, 61, 62]), LiF (Mg2+ [11, 63]) and AgCl (Pb2+ [64]) and even in oxides (MgO:Mn4+ [31], [65]–[67], NiO:Mn4+ [67] and CuO:Pb4+ [32, 68]). Suzuki phases including two types of metal impurity cations have even been studied (NaCl:Pb, Eu2+ [69] and NaCl: Cd, Pb2+ [70]).

The Suzuki phase has been characterized by many experimental methods like x-ray diffraction [10]–[12], [31, 32], [34]–[36], [38, 58, 65, 67], ionic conductivity or thermal current measurements [21, 35, 37, 39, 52, 54, 66], specific heat measurements [47], optical spectroscopy [46, 50, 53, 56, 59, 60, 62, 65, 67, 69, 70], Raman spectroscopy [12, 40, 52, 53, 55], laser spectroscopy [57], magnetic susceptibility measurements [41, 48, 65, 67], electron paramagnetic resonance [45, 46, 60, 64], neutron scattering [49], photoacoustic measurements [61, 62] and Mössbauer spectroscopy [51]. Optical [11, 14] and electron transmission microscopy [11]–[21] have been used to visualize the Suzuki precipitates on surfaces and in bulk at the micrometre and the nanometre scale, respectively. A characterization at the atomic scale has recently been done by dynamic SFM [1]. From the theoretical point of view, some works can be found that deal with the formation [41, 42, 63], [71]–[73] and with the stability of the Suzuki phase [43, 44, 68].
Although the size of the unit cell of the Suzuki phase can be measured by x-ray diffraction with high precision, slightly deviating values for its size can be found in the literature. For NaCl:Cd$^{2+}$ crystals, a size between 11.248(3) Å [36] and 11.278 Å [38] has been reported, which is slightly smaller than the value of 11.39(1) Å calculated for 0 K [43, 44]. The experimental values show that the Suzuki unit cell is not exactly twice as large as the unit cell of NaCl ($a_{NaCl} = 5.64$ Å, $a_{Suzuki/2} = 5.624$ Å [36] and $a_{Suzuki/2} = 5.639$ Å [38]). Kazuo Suzuki has already shown from his x-ray diffraction experiments that the Cl$^{-}$ ions relax towards the Cd$^{2+}$ ions in the (001) surface plane [10], whereas the Na$^{+}$ and Cd$^{2+}$ ions stay on the regular sites of the NaCl structure. In the literature, different values for the relaxation $\delta$ (fraction of $a_{Suzuki}$) of the Cl$^{-}$ ions can be found ($\delta = 0.028$ [10], 0.014 [34], 0.020 [71] and 0.0154 [43]). The average of the latter values ($\delta = 0.19$) exemplifies that the Cl$^{-}$ ions relax 0.2 Å towards the Cd$^{2+}$ ions in the (001) surface plane.

3. Experimental methods

Dynamic SFM and KPFM experiments were performed in the low $10^{-10}$ mbar pressure range and at room temperature with an Omicron STM/AFM (a digital demodulator from NanoSurf). Different conducting silicon cantilevers (Nanosensors, p-Si, 0.015 $\Omega$ cm, 37 N m$^{-1}$ spring constant) were used. Because the tips were originally exposed to the atmosphere, the tips carried a native oxide layer before taking measurements.

In frequency-modulated KPFM, a dc ($U_{dc}$) and an ac voltage ($U_{ac}$) with frequency $f_{ac}$ are applied on the rear side of the sample [74, 75]. The tip is grounded. In such a measurement, the electrostatic tip–surface interaction is minimized at each point on the surface by the bias voltage $U_{dc,0}$. In the case of an insulator, the work function between the tip and the metallic sample holder in the presence of the insulator is measured [76], which is, however, strongly modified by surface charges. In most cases, the surface charge distribution determines the Kelvin contrast [28]. The Kelvin modulation is applied during the normal topography imaging so that a topography and a Kelvin image ($U_{dc,0}$) are obtained at the same time in one Kelvin measurement. Images were acquired with the Omicron SCALA system and prepared with the WSxM software [77].

The doped NaCl crystals were grown in an argon atmosphere by the Czochralski growth method [20]. The melt contained a few molecular per cent of CdCl$_2$. The crystals were stored for years in air and at room temperature and were milky before their use, which is a signature for the presence of Suzuki precipitates inside the material [34, 55]. In the case of a large doping level ($\sim 4–5$ mol% CdCl$_2$), precipitates could even be observed with a standard optical microscope (e.g. Zeiss Ultraphot) at large magnification as was reported earlier [14]. All (001) surfaces were prepared by UHV cleavage at room temperature, whereas some crystals were additionally annealed in a UHV oven [78]. The cleavage and SFM were done in the same UHV chamber [78].

4. As-cleaved crystals

After UHV cleavage of an alkali halide crystal, the new surface is not in its equilibrium charge state [80], and newly created defects like dislocations, which are sinks or sources for e.g. charged vacancies [79], or already existing charged defects (e.g. impurities) charge the crystal surface. This surface charge stays for a relatively long time for pure alkali halide crystals [75] and creates a strong electrostatic tip–surface interaction, which can be detected even at several
Figure 2. Suzuki precipitates on the (001) surface of an as-cleaved NaCl:Cd\(^{2+}\) crystal (4 mol\% of CdCl\(_2\)). Shown are the topography (a) and Kelvin image (b). (c) Profile taken at the white line in (b): 2 × 2 \(\mu\)m\(^2\), \(\Delta f = -15.7\) Hz, \(A_{p-p} = 19.5\) nm, \(f_{ac} = 474\) Hz and \(U_{ac} = 1.4\) V.

tens of nanometres distance [75]. Dynamic SFM imaging is difficult to perform. The crystals must be kept for a couple of days at room temperature or they must be annealed within one hour at \(\sim 100\) °C so that the charges flow off and the crystal is in its equilibrium charge state [28, 75]. In contrast, dynamic SFM measurements can be immediately performed after the UHV cleavage of doped crystals where no strong surface charging exists after one hour of the cleavage.

It is obvious that these differences between pure and doped crystals are related to the ionic conductivity of both types of materials: the higher the conductivity, the faster the reduction of the charge. For pure crystals, an ionic conductivity between \(10^{-16}\) and \(10^{-14}\) \(\Omega^{-1}\)cm\(^{-1}\) can be found at room temperature (exponential extrapolation of the high-temperature data in [81]), which is much smaller than that for Cd\(^{2+}\)-doped NaCl crystals (\(\sim 10^{-10}\) \(\Omega^{-1}\)cm\(^{-1}\) [37, 39]). The higher ionic conductivity of doped crystals can be observed within a large temperature range, even at temperatures higher than room temperature [35, 54].

Figure 2 shows typical characteristics of the (001) surface after the UHV cleavage of an NaCl:Cd\(^{2+}\) crystal, which was doped with 4 mol\% of CdCl\(_2\). The crystal was not additionally annealed after the cleavage. In the middle of the topography, image (a), two 400 × 400 nm\(^2\) large quadratic Suzuki precipitates can be found, which are surrounded by regions of pure NaCl(001). The precipitates appear in the form of depressions, whereas their edges are oriented along equivalent (100) surface directions as observed before on surfaces of as-cleaved crystals [16, 19]. The square shape of the precipitates in figure 2 is in fact the projection of their 3D shape in the bulk, which is cubic in most cases [18, 19]. Only one work reports that \{111\} facets may also partially form the 3D shape of precipitates [21]. The large size of the precipitates is probably due to a slow cooling, which was accomplished after the crystal growth [20], and due to the long storage of the crystals in air and at room temperature for several years. As explained before, such conditions produce especially large precipitates in the bulk [12, 21, 34].

The Kelvin image (b) in figure 2 exhibits a strong bright contrast with respect to the NaCl regions (dark), which corresponds to a voltage difference of \(\sim 1.3\) V (see figure 2(c)), which is comparable with values found at Suzuki precipitates on NaCl:Mg\(^{2+}\)(001) surfaces [1]. Due to
the large Kelvin contrast at precipitates, two other precipitates of much smaller size can be immediately found at positions 1 and 2, which are less visible in the topography image (a). As was found on the MgO:Mg$^{2+}$(001) surfaces, the Kelvin contrast is homogeneous inside the Suzuki precipitates and no further details can be obtained even by choosing smaller scanning frames. For Suzuki-terminated Suzuki surfaces, a homogeneous bright Kelvin contrast was explained by the high density of the Na$^+$ vacancies, which deliver to the precipitates a net negative surface charge (bright contrast) [1]. Because the tip apex has a size between $\sim$5 and 50 nm, the tip integrates the electrostatic tip–surface interaction over a surface region that is comparable with the size of the tip apex comprising many Na$^+$ vacancies. This explains not only the homogeneous contrast but also the high voltage of 1.3 V. In contrast, single Na$^+$ vacancies at steps in pure NaCl(001) regions, which can be found in the vicinity of the precipitates, produce a considerably lower bright contrast of $\sim$300 mV (compare contrast values in figure 2(c)) in agreement with earlier findings [28].

If the Suzuki surface is NaCl-terminated (figure 1(d)), Cl$^-$ ions are located above the Na$^+$ vacancies and stick out from the surface by about 40 pm. Because these Cl$^-$ ions have in a way a lower coordination with respect to other Cl$^-$ ions of the same layer, they are comparable with Cl$^-$ ions at kinks of steps. As explained in [28], a more negative net charge is measured by KPFM also in this case. Note that all Kelvin images taken to date exhibited only a bright contrast at Suzuki precipitates and at the steps of NaCl. This means that also the surfaces of NaCl: Cd$^{2+}$ crystals carry a net negative surface charge, which is probably due to a mechanism similar to the surface double layer mechanism [28, 72, 82].

In contrast to the flat precipitates observed before by dynamic SFM on MgO:Mg$^{2+}$(001) surfaces [1] and further described in section 5, several steps can be found inside the Suzuki precipitates here, which can be best seen in figure 3(b). The histogram (figure 3(c)) shows the distribution of the step heights in the region of the dotted square of figure 3(b). Only steps with

**Figure 3.** Topography images (a, b, d) of the steps in the Suzuki precipitates and NaCl regions shown in figure 2. (c) Histogram representing the step height distribution of the region marked by the rectangle in (b). (a, d) 645 × 590 nm$^2$, $\Delta f = -21.0$ Hz, $f_{ac} = 474$ Hz, $U_{ac} = 1.4$ V; (b) 650 × 525 nm$^2$, $\Delta f = -15.7$ Hz; (a–d) $A_{p-p} = 19.5$ nm.
a height of 5.6 Å can be found, which corresponds to $1/2 \times a_{\text{Suzuki}}$ (figure 1(c)). This implies that all terraces are either NaCl-terminated Suzuki surfaces (figure 1(d)) or Suzuki-terminated Suzuki surfaces (figure 1(e)).

Remarkable is the course of the steps in the NaCl regions, which are partially continued inside the Suzuki precipitates and vice versa (see figure 2(a)). From left to right, which was in fact the direction of the incoming cleavage crack during the cleavage, the steps in the NaCl region turn their direction clockwise by $\sim 20^\circ$ inside the left precipitate, recover their original direction on NaCl in between the two precipitates and turn their direction clockwise again inside the right precipitate. After the latter precipitate, they change their direction again. If the steps in the NaCl regions in between the two Suzuki precipitates (figure 3(b)) and at the right border of the right large precipitate (figure 3(d)) are analysed in more detail, a part of the steps can be found that are almost horizontal and parallel to equivalent $\langle 100 \rangle$ surface directions. Some of them form cleavage tips (e.g. at position 1 in figure (d)) with steps, which follow the mean step direction in the NaCl(001) region around the two precipitates (compare with figure 3(a)). The latter steps are inclined by $10^\circ$ with respect to the $\langle 100 \rangle$ steps.

Steps emanating at Suzuki precipitates into NaCl/(001) regions have already been observed before by TEM on the surfaces of different as-cleaved NaCl material (NaCl:Cd$^{2+}$, Mn$^{2+}$, Fe$^{2+}$) [13], [17]–[19]. The specific step structure is a result of the cleavage crack, which cuts $\langle 110 \rangle$ screw dislocations at the Suzuki–NaCl interface, leaving $\langle 100 \rangle$ slip steps in regions of NaCl behind. Because the unit cell of the Suzuki phase is not exactly twice that of the NaCl unit cell ($a_{\text{NaCl}} = 5.64$ Å and $a_{\text{Suzuki}}/2 = 5.624$ Å [36]), the dislocations are a result of the small misfit and release the related strain at the interface [18]. The $\langle 110 \rangle$ screw dislocations lie in the $\{110\}$ planes, which intersect the $\{001\}$ planes and which are the slip or gliding planes in pure NaCl [83]–[85]. The steps, which are inclined by about $10^\circ$ with respect to the $\langle 100 \rangle$ steps, are probably local cleavage steps.

The reason for the specific step direction inside the Suzuki precipitates remains unknown so far. It can be speculated that, in this case, dislocations at the interface, where the cleavage crack enters the precipitates from NaCl regions, also play a major role. On the other hand, a simple explanation would be that the steps adapted the mean cleavage direction of the complete surface region. The mean cleavage direction is represented by the nanometre high cleavage step $s_1$ in figure 2(a). This step is composed of many merging cleavage steps ending up in one single step with a height of 3.8 nm, which is parallel to the steps inside the precipitates.

Some TEM images show equidistant $\langle 110 \rangle$ steps (ledges) inside the Suzuki precipitates (see TEM images in [19]). The steps have a very small step–step distance of 10 nm and below and change alternately their sign. It was concluded that these small step–step distances cannot result from perfect $\langle 110 \rangle$ screw dislocations [19]. The authors anticipated that the steps are a result of the alternating expansions and contradictions of the Cl$^-$ ions, which appear around the Cd$^{2+}$ ions along the $\langle 110 \rangle$ directions. These alternating strains are then relieved by partial $\langle 110 \rangle$ screw dislocations, which have a magnitude of the Burgers vector of $\sqrt{2} \cdot \delta \cdot a_{\text{Suzuki}}$ [19]. With the much higher lateral resolution of the SFM, these types of steps could be clearly imaged in another Suzuki precipitate that was found in the vicinity of the precipitates from above (figure 2). The topography (a) in figure 4 shows two monoatomic high steps on the pure NaCl/(001) surface, which adjoin the left border of the precipitate. The upper step $s_2$ penetrates the precipitate and turns its surface direction clockwise being almost parallel to the step $s_1$ in the surface region discussed before (figure 2(a)). Inside the Suzuki precipitate nanometre-thick trenches can be found (figure 4(c)), whose edges are inclined to the step $s_2$ and roughly oriented along the
Figure 4. A Suzuki precipitate found on the same crystal surface as in figure 2 (4 mol% of CdCl$_2$). (a) Topography image and (b) corresponding Kelvin image. (c) Topography image showing a larger magnification of the lower part of the precipitate. The Kelvin image (b) exhibits only a contrast change of 270 mV between the precipitate and pure NaCl regions, which is lower than the Kelvin contrast measured at the precipitates in figure 2. The reason for this is that the new tip used here had a smaller tip apex than the tip used for the measurements shown in figure 2. The tip apex integrated over fewer negative vacancies. (a, b) 470 × 620 nm$^2$, Δ$f = -6.5$ Hz; (c) 355 × 240 nm$^2$, Δ$f = -10.0$ Hz; (a–d) $A_{p-p} = 8.0$ nm, $Δf = -6.5$ Hz, $f_{ac} = 474$ Hz and $U_{ac} = 1.4$ V.

{$\langle 110 \rangle$}-direction. The trenches exhibit a mean distance between 5 and 10 nm, which agrees with the TEM observations from above.

A striking observation is the depth of the trenches, which corresponds to half of the NaCl unit cell ($h = 1/2a_{NaCl}$). The two Suzuki terraces are separated by half of the Suzuki unit cell ($h = a_{NaCl} = 1/2a_{Suzuki}$), which means that both of them are either Suzuki- or NaCl-terminated surfaces. The bottom of the trenches of one terrace have then the opposite termination to the terrace. Because the surface of the Suzuki precipitate is stable (e.g. no changes during scanning), it shows that both surface terminations, the NaCl-terminated and Suzuki-terminated Suzuki surface, may coexist at the same time. Indeed, recent calculations support this and show only little differences in the surface energy between both surfaces [33].

5. Surfaces created by surface diffusion

5.1. Appearance of Suzuki precipitates

If pure alkali halides, such as NaCl, are annealed in vacuum at temperatures between 200 and 260 °C, the mobility of the surface ions is already large enough to change significantly the
Figure 5. The NaCl:Cd$^{2+}$(001) surface created by surface diffusion processes (4 mol% CdCl$_2$, $T = 230^\circ$C for 5 h). In order to put the crystal surface into its equilibrium state, the annealing and cooling were done slowly with a speed not higher than 6 $^\circ$C min$^{-1}$. (a) Topography and (b) the corresponding Kelvin image $600 \times 410$ nm$^2$, $A_{p-p} = 8.0$ nm, $\Delta f = -18.72$ Hz, $f_{ac} = 484$ Hz and $U_{ac} = 1.5$ V.

surface topography [86]. This can be observed especially at steps [86]. At temperatures larger than $\sim 260^\circ$C, the surface starts to evaporate [87]–[89], creating well-documented surface evaporation patterns [23, 88]. In view of NaCl crystals, which are doped with divalent metal impurity cations, the presence of the impurities decreases the evaporation rate and increases the activation energy of evaporation [90].

The measurement in figure 5 shows a surface that was created by surface diffusion processes (4 mol% CdCl$_2$ at 230 $^\circ$C for 5 h). If the surface is compared with the surface of the as-cleaved crystal in figure 2, the influence of the surface diffusion becomes immediately evident: during the annealing the large, rectangular precipitates on as-cleaved surfaces disappear and smaller precipitates are formed at all steps and partially on the flat terraces. Never were $400 \times 400$ nm$^2$ large rectangular or quadratic precipitates observed after the annealing of crystals doped with 4 mol% CdCl$_2$. This shows that an annealing at these temperatures leads to a large mass transport on the surface. However, not only is mass transported on the surface but it is also expected that impurities segregate from the bulk to the surface [91], which enriches the surface with Suzuki precipitates. Tentatively, dynamic SFM measurements performed on a couple of different crystal surfaces support the latter.

The size and number of Suzuki precipitates depend on, e.g. the annealing time [16], the speed of cooling (bulk [12, 34] and surface [17]) and certainly on the nominal amount of impurities inside the crystal [20]. For instance, more precipitates can be found on the surface if the cooling is accomplished in a slow manner. Furthermore, the higher the impurity amount the more precipitates can be found on the surface (compare the surface in figure 5 (4 mol% CdCl$_2$) with the surface in figure 6 (1 mol% CdCl$_2$)).

The location and shape of the precipitates strongly depend on the step density: the topography (a) and Kelvin image (b) in figure 6 show precipitates at the monoatomic high steps ($h = 1/2a_{NaCl}$) forming a fringe with a characteristic zigzag shape but also rectangular precipitates on flat terraces. In such surface regions the step density is relatively low. In surface regions with a higher step density, only precipitates at steps can be found and no rectangular precipitates appear on the flat terraces. An example is given by the measurement (c) and (d),
Figure 6. NaCl:Cd\(^{2+}\)(001) surfaces which were created by surface diffusion (1 mol\% CdCl\(_2\), \(T = 205^\circ C\) for 5 h). Images (a) and (c) are topography images and images (b) and (d) are the corresponding Kelvin images. All steps are monoatomic high steps (1/2\(a_{NaCl}\)). The topography image (a) shows a depression for some pm at the precipitates, which is a result of the Kelvin regulation where the bias voltage \(U_{dc}\) did not fully minimize the electrostatic tip–surface interaction. Sometimes a precipitate appears also as an elevation due to the same reasons, which can be seen in image (c). (a, b) 600 \times 600 \text{nm}^2, (c, d) 400 \times 360 \text{nm}^2; (a–d) \(A_{p-p} = 15.4 \text{ nm}\), \(\Delta f = -7.3 \text{ Hz}\), \(f_{ac} = 478 \text{ Hz}\) and \(U_{ac} = 1.5 \text{ V}\).

which was recorded on the same surface but some microns away from the surface region shown in images (a) and (b). From measurements performed on many surfaces, it follows that rectangular precipitates can be found on terraces with a width larger than 150–200 nm. Although the reason for this is unknown to date, it can be anticipated that the nucleation of the impurity ions and vacancies into Suzuki precipitates is obviously energetically more favorable at steps than on the flat terraces. This is supported by the observation that Suzuki precipitates can always be found at steps. However, if the steps are far away not only from each other but also from a Suzuki nucleation germ on the flat terrace, rectangular precipitates will be created on the flat terraces as well.

A very important characteristic of annealed surfaces is that no steps can be found inside the precipitates in contrast to the steps observed on as-cleaved crystal surfaces (section 4). Because the cooling is slowly accomplished after the annealing of the crystal, the surface is put into
its equilibrium state. This means that, although the steps inside the precipitates on as-cleaved crystal surfaces are stable at room temperature, the minimum equilibrium state of a Suzuki surface is, however, a flat surface. It can be further anticipated that during the annealing, the surface system searches for an equilibrium state for the precipitates such that not much strain at the Suzuki–NaCl interface is created and released by dislocations, which would cost energy. This probably explains why the precipitates are then smaller after the annealing because the mismatch between the NaCl and Suzuki structures does not play such a large role [12, 34]. Furthermore, in the case of a large amount of impurity inside the crystal, not much space is left on the surface for the creation of small precipitates. It can be assumed that the surface system then adapts the Suzuki–NaCl borders such that they get curved as can be seen in figure 5.

5.2. Suzuki precipitates at the atomic scale

Dynamic SFM images with atomic resolution can be easily obtained on Suzuki precipitates as exemplified by the constant height image (a) in figure 7. The image was recorded in a Suzuki precipitate without the Kelvin modulation technique. Dark spots can be seen (e.g. at position 1), which form a sublattice that corresponds either to the Na\(^+\) vacancies or Cd\(^{2+}\) impurities (a dark contrast corresponds to more negative detuning values \(\Delta f\) and vice versa). Another distinct sublattice of bright ions can be seen (e.g. at position 2), whose size equals that of the smallest possible sublattice in the Suzuki structure. As is shown in another work [33], this specific atomic contrast can only be created by a tip with a positive potential (e.g. an Na\(^+\) terminated tip), which images the NaCl-terminated Suzuki surface. The dark and bright spots then belong, in fact, to the Cl\(^-\) ions above the vacancies of the second layer and to the Na\(^+\) ions above the Cl\(^-\) ions of the second layer (figure 7(b)), respectively [33].

Figure 7(c) exemplifies that, in principle, both surface regions (pure NaCl and Suzuki) can be imaged with atomic resolution within one image. In the lower left part of the image, the pure NaCl(001) surface can be seen, whereas the region outside the pure NaCl(001) region belongs to a Suzuki region. Both regions exhibit the same contrast colour, which means that both are on the same height level. The bright (110) sublattice in the NaCl region is formed either by the Cl\(^-\) or Na\(^+\) ions and is considerably smaller with respect to the one that is formed by dark spots in the Suzuki region. The lattice of the latter dark spots is oriented towards equivalent \(\langle 100 \rangle\) directions and has the exact size of the sublattice formed by the Na\(^+\) ions in the layer of the Cd\(^{2+}\) ions and Na\(^+\) vacancies (figure 1(e)).

In the literature, some attention has been paid to the direct observation of dislocations at precipitates. Dislocations could indeed be observed in the bulk by TEM [18, 19, 21]. The TEM images show straight but also curved dislocations emanating from the precipitates, but no precise information such as the Burgers vector could be gained [18, 21]. This is, however, possible with the force microscope at the atomic scale as exemplified by the constant height image (d) in figure 7 (see the region inside the dotted rectangle). A vertical line defect along the \([100]\) direction can be seen, where no atomic resolution could be obtained. Because figure 7(d) was obtained above the surface region shown in figure 7(c), the line defect can be followed at the Suzuki–NaCl interface, which is marked by the dotted grey rectangle in figure 7(c). The bright dotted lines in both images (figure 7(c) and (d)) clearly show that the rows of bright spots on the left side of the line defect hit the rows of dark spots on the right side. An analysis of both images (figure 7(c) and (d)) shows that the sublattice of the dark spots on the left side of the line defect is shifted by 1/2 of its size \((1/2 \ a_{Na,S})\) along both equivalent \(\langle 100 \rangle\) directions with respect to the same lattice on the right side of the line.

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Figure 7. (a) Constant height image with atomic resolution recorded inside a Suzuki precipitate. (b) Drawing representing the \(\text{Cd}^{2+}\) ions and vacancies of the second (Suzuki) layer. (c, d) Constant height images representing both regions (NaCl and Suzuki) and a dislocation line in atomic resolution. (e) A possible atomic configuration of the dislocation line. The shift of the lattices on each side of the dislocation is represented by the black arrow. (a) \(2.9 \times 2.5\ \text{nm}^2\), \(\Delta f = -115.0\ \text{Hz}\); (c) \(10 \times 4.4\ \text{nm}^2\), \(\Delta f = -37.3\ \text{Hz}\); (d) \(9.2 \times 6.3\ \text{nm}^2\), \(\Delta f = -37.3\ \text{Hz}\); (a–e) \(A_{p-p} = 15.4\ \text{nm}\).

The line defect is in fact a dislocation as shown in figure 7(e), which represents a possible atomic configuration of the surface area shown in figure 7(c) and (d). The dislocation is probably a \(\{100\}\) \(\langle 100 \rangle\) screw dislocation (follow grey dotted lines in figure 7(e), which symbolize the ‘screw-like character’), whose Burgers vector points in the \([100]\) direction and which lies in the \((001)\) surface plane. Note that if the Na\(^+\) vacancies and Cd\(^{2+}\) ions are replaced by Na\(^+\) ions, the perfect NaCl\((001)\) surface is gained without any dislocation. This is in agreement with the general picture that dislocations are \(\{011\}\) \(\langle 1\bar{1}0 \rangle\) dislocations in NaCl \([83]–[85]\). The type of dislocation found here is therefore a specific characteristic of the atomic Suzuki structure.

Alongside the shape, nucleation and flatness of precipitates on annealed surfaces, the steps exhibit quite interesting characteristics as well: the borders, which divide precipitates and NaCl regions at the same height level, form characteristic zigzag shapes with straight sections along equivalent \(\langle 100 \rangle\) directions (see the \([100]\) arrow in figure 8(a)). Note that the precipitates are located only on the top of the steps but not at the bottom (see the three regions NaCl–Suzuki–NaCl in figure 8(a)), which is a striking difference to NaCl:\(\text{Mg}^{2+}\)\((001)\) surfaces where precipitates adjoin the step also from the bottom (compare with figure 1 of [1]). If the step edges are analysed, their zigzag shape is composed of straight sections, that are oriented towards equivalent \(\langle 110 \rangle\) directions (see the \([110]\) arrow in figure 8(a)). This was verified by constant height images at atomic resolution (figure 8(b)). The sublattice of either the Na\(^+\) vacancies or Cd\(^{2+}\) impurity ions can be clearly seen on the upper terrace (small black square). The \(\langle 110 \rangle\) step direction is sometimes changed by kinks as observed at position 1 in figure 8(c). A kink here corresponds to one cell of the sublattice, which is composed of the Na\(^+\) vacancies or Cd\(^{2+}\)
impurity ions and which is a change of position by $\alpha_{V, Cd}$. At some kinks a strong bright contrast change can be observed (e.g. position 2 in figure 8(b)) which was probably produced by defects at the kinks. The change of the step direction by kinks realizes, on the one hand, that the $\langle 110 \rangle$ step direction is conserved at the small nm scale and, on the other hand, that the steps may appear round at a much larger scale (see e.g. figure 6(c)).

The reason for the $\langle 110 \rangle$ direction of the steps is as much unknown as the exact composition of the step forming ions, where the Na$^+$, Cl$^-$, Cd$^{2+}$ or the Na$^+$ vacancies can be found in principle. Besides, the finding of $\langle 110 \rangle$ steps is surprising because these are polar steps, which are normally less favored on (001) surfaces of pure NaCl than neutral $\langle 100 \rangle$ steps [92]. The steps were not produced by cleavage and are a result of the annealing and the following cooling that was slowly accomplished. This means that the $\langle 110 \rangle$ step configuration has the smallest formation energy in comparison to all possible step configurations along other directions. In order to understand this, numerical calculations as presented in [92] must be carried out.

6. Surfaces created by surface evaporation

Figure 9 illustrates the main characteristics of surfaces, which are created by surface diffusion and notably evaporation processes. The Kelvin measurement (figures 9(a) and (b)) was recorded on the surface of a doped NaCl crystal, which included 2 mol% of CdCl$_2$. The crystal was annealed at 340 °C for 30 min and quickly cooled down afterwards in order to freeze the evaporated surface. Note that the cooling was sufficiently quick to freeze the surface but also slow enough to guarantee that the Suzuki precipitates, which disappear at temperatures larger than 300 °C [34, 35], reappear during the cooling [38].
Figure 9. NaCl: Cd$^{2+}$ (001) surfaces, which were created by surface evaporation during annealing at 340 °C for 35 min. (a, b) Large-scale image showing characteristic evaporation patterns. (c, d) Images with a larger magnification. Images (a) and (c) are topography images and images (c) and (d) are the corresponding Kelvin images. (a, b) 800 × 800 nm$^2$, $\Delta f = -9.3$ Hz, $A_{p-p} = 15.4$ nm; (c, d) 150 × 150 nm$^2$, $\Delta f = -18.8$ Hz, $A_{p-p} = 8.0$ nm; (a–d) $f_{ac} = 474$ Hz, $U_{ac} = 1.4$ V.

The topography image shows almost curved monoatomic high NaCl steps ($h = a_{NaCl}/2$) in the upper part of the image and circular ones at the bottom. The steps belong in fact to disc-shaped holes, which are known to be created by evaporation on surfaces of pure NaCl at similar temperatures [88]. For pure NaCl crystals, evaporation takes place at dislocations [88], which is probably the same here. A more detailed analysis of the step structure reveals that the (001) surfaces of doped NaCl slightly differs from that of pure NaCl. The measurement below (figures 9(c) and (d)) shows that the steps are not as smooth as can be observed on surfaces of pure NaCl or KCl [23, 88]. The topography images (a) and (c) show that the steps exhibit rather a zigzag shape, which is curved on a larger scale, forming the disc-shaped holes. Note that as before (section 5.1) the steps are oriented along equivalent ⟨110⟩ surface directions, whereas the borders of embedded precipitates point along equivalent ⟨100⟩ surface directions. The Kelvin images (b and d) prove that Suzuki precipitates form the edges of the steps. It can therefore be concluded that, although the main evaporation characteristics seem to be the same as for pure NaCl, the impurities locally modify the surface topography at steps.
An important observation is that no embedded rectangular Suzuki precipitates appear on large atomically flat terraces, where both the NaCl(001) surface and the one of the precipitate are on the same height level. This becomes evident when, e.g., the large terrace at position (1) in figure 9(a) is inspected: the terrace has a width larger than 200 nm. The reason could be that impurities on flat terraces are germs for the evaporation of the surface so that finally no embedded rectangular precipitates are formed. Indeed, a pit can be found on the terrace at position 1. In contrast, rectangular precipitates on pure NaCl(001) terraces can be found, which exhibit, however, a height of one monolayer of NaCl \((h = a_{\text{NaCl}}/2)\). One rectangular island can be seen, e.g. at position 1. Because this island and others are close to the steps, it seems that they once belonged to the step before diffusion and evaporation processes separated them. A similar observation has been made on (001) surfaces of pure NaCl [86].

7. Conclusions

A UHV dynamic SFM and Kelvin microscopy study of Suzuki precipitates on NaCl: Cd\(^{2+}\) (001) surfaces is presented here for the first time. The appearance of the precipitates on three different types of surfaces is discussed: precipitates on as-cleaved surfaces and on surfaces which were produced either by surface diffusion or surface evaporation processes, during additional annealing of the crystals.

On as-cleaved surfaces, \(400 \times 400 \text{ nm}^2\) large rectangular Suzuki precipitates could be found. The precipitates exhibit steps with a height corresponding to half of the Suzuki unit cell but also smaller, equidistant steps along the \(\langle 110 \rangle\) surface directions. Steps at and inside the precipitates are created by cutting dislocations at the Suzuki–NaCl interface during the cleavage. On annealed surfaces, which are changed by surface diffusion processes, the precipitates are atomically flat. Rectangular precipitates can only be found in surface regions with a step–step distance larger than 150–200 nm, whereas precipitates can be always found at steps. The steps prefer equivalent \(\langle 110 \rangle\) directions, which seems to be the equilibrium orientation. On surfaces, which are influenced by surface evaporation processes, the same evaporation structures as those found on pure NaCl(001) surfaces can be observed. The impurities in NaCl: Cd\(^{2+}\) merely change the edge of steps at the nanometre scale by creating a characteristic zigzag shape of Suzuki precipitates. No rectangular precipitates could be found even on large terraces.

It is strongly believed that Suzuki surfaces deserve a renaissance in that they are used as potential templates for the deposition of nano-objects like molecules or metal nanoclusters. The work presented here gives an overview of the three types of surfaces and animates the use of nanostructured Suzuki surfaces in nanotechnology.

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