

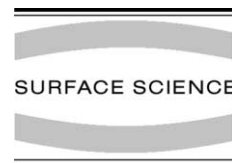


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Growth and characteristics of the $\{111\}$ NaCl crystal surface grown from solution

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Abstract

The morphology of $\{111\}$ faces grown from water–formamide solutions as well as from pure water solutions was investigated. Surface patterns were examined ex situ and in situ using bright field and differential interference contrast optical microscopy and ex situ atomic force microscopy. It was shown that formamide and urea stabilize the $\{111\}$ NaCl faces, whereas larger homologous molecules do not. For the $\{111\}$ NaCl crystals growing from water–formamide solutions, it was observed that growth proceeds by monomolecular, stabilized layers of height $d_{\{111\}}$, with most probably Na^+ ions on top of Cl^- ions. Steps originate from spiral-dislocation growth as well as from 2D nucleation starting from the edges of the crystal. Atomic resolution imaging of NaCl $\{111\}$ showed no surface reconstruction. The $\{111\}$ surfaces grown from pure water solutions showed developing of shallow growth hillocks with rounded tops. It is presumed that these hillocks are related to dislocation outcrops and growth proceeds close to the roughening temperature. Growth pits develop after a longer period of $\{111\}$ surface growth in water solution. Their formation is explained by the presence of a semipermeable particle at the pit bottom, which locally retards the fast $\{111\}$ growth.

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1. Introduction

Growth of a $\{111\}$ polar surface of a crystal with rocksalt structure has been one of the attractive themes in the fields of crystal growth and surface science. The history goes back to 1783, when Rome de l'Isle showed that octahedrons instead of normal cubes are formed, if rocksalt is

grown in the presence of urine [1]. Despite more than two centuries since this discovery, the electrostatically polar $\{111\}$ surfaces of the NaCl crystal structure were long considered a mystery in surface science, because they are difficult to investigate both experimentally and theoretically. Since the bulk structure consists of alternating cationic and anionic sheets stacked along the $\langle 111 \rangle$ directions, the $\{111\}$ surfaces must have a very high divergent electrostatic energy, which makes them theoretically highly unstable [2]. Therefore, the form $\{111\}$ is not expected to occur on the morphology of NaCl-type crystals. However, if such a

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flat, well-ordered (111) surface can be obtained, several interesting properties, such as novel catalytic activity or a two-dimensional electron system on top of an insulating crystal might be expected [3].

In this context, the growth of {111} surfaces has been examined for various highly ionic materials. Most detailed information was obtained for solid-vacuum systems. In the recent past, the (111) surface of rocksalt structure NiO was the most extensively studied case. Langell and Berrie grew NiO on Ni (100) and (111) substrates by oxidation and characterized the grown film (three monolayers thick) by low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS) [4]. They found that the NiO (111) surface is stabilized by OH adsorbates and that desorption of the hydroxyl resulted in a change of the surface into a thermodynamically more stable NiO (100) thin film. Stabilization by impurities was also found for Pb [5] and Si [6] on NiO (111). Ventrice and co-workers grew NiO on an Au (111) substrate and observed the grown film by LEED and scanning tunneling microscopy (STM) [7,8]. Their results showed the existence of an epitaxial $p(2 \times 2)$ overlayer structure of 55 nm domain size, which they ascribed to a periodic arrangement of octupolar $(\text{NaCl})_4$ basic units. The stabilization of the {111} NaCl surface by octupoles, each consisting of one unit cell, was proposed by Lacmann, more than 35 years ago [9]. Wolf confirmed this “octupole” reconstruction hypothesis, which cancels the divergence of the electric field in the crystal, by calculations for the {111} NaCl surface in contact with vacuum [10]. Saiki et al. obtained the flat (111) NaCl surface for the complex heterostructure of NaCl/CuCl/CuBr/GaAs(111)Ga 2×2 , which, in contrast to the previous results for the NiO (111) surface, was stable even for the thick films [11]. They found no reconstruction. Finally, using atomic force microscopy (AFM), Hegenbart and Müssig observed two additional reconstructions, namely an orthorhombic and a hexagonal one on the (111) surface of AgBr, which is isostructural with NaCl [12].

The above work only concerns with solid-vacuum systems. A major effort has also been made in

investigating the occurrence of NaCl {111} faces during growth from aqueous solutions. Bienfait et al. [13] investigated the occurrence of the octahedral faces for a wide range of supersaturations and impurities. Surface topography, using ex situ optical microscopy of {111} KCl surfaces obtained after growth in the presence of metal ion impurities, showed the occurrence of growth hillocks and macrosteps [14]. As far as known to us, no optical microscopy or AFM work was carried out for {111} NaCl, but Nozoye and Takdo found no reconstruction on the {111} faces of AgBr [15]. Plomp et al. [16] observed steps of height $1/3 \langle 111 \rangle$ on the {111} faces of the same crystal, but now grown from a DMSO solution.

In our laboratory we were able to grow octahedral NaCl single crystals of several millimeters to one centimeter in size with large, flat and stable {111} faces. This opens possibilities to investigate the surface structure of these faces by optical microscopy and AFM in a convenient way. In the present paper we describe the growth and characteristics of the (111) NaCl crystal surface grown from solution.

2. Experimental procedure

The octahedral crystals used for the experiments were grown from a filtrated ($0.45 \mu\text{m}$ pore width), nearly saturated aqueous NaCl solution in which 20–30 wt.% of formamide was added. The crystals were obtained by slow evaporation of this solution in a desiccator with concentrated sulfuric acid as drying agent placed at the bottom of the desiccator [17]. We then selected specimens with a size of about $5 \times 5 \times 3 \text{ mm}^3$, with very flat {111} faces on the top and sides. Generally, these crystals are relatively free from liquid inclusions. Apart from quick drying using a paper tissue after separation from the growth solution, no further surface treatment was applied prior to surface examination. The surface patterns did not change when kept dry in a desiccator and were quickly observed after removal from it. In order to get insight into the mechanism of stabilization of the {111} face by formamide and to ascertain whether we can produce similar effects, i.e. the ap-

pearance of $\{111\}$ faces, instead of formamide we also added homologous compounds to our growth NaCl–water solution, such as urea, dimethylformamide and benzamide.

In some experiments we submerged an octahedral NaCl crystal into a slightly supersaturated solution of NaCl in pure water or placed a droplet of the same solution on the (111) face for 15–30 min at room temperature to observe the growth features in situ as well as ex situ. In this way the influence of the water molecule on the stabilization of the (111) face is established. To determine the presence of dislocations in the NaCl crystals, the $\{111\}$ planes were etched using formamide. Etching was performed by placing a droplet of formamide (purity 99.5%) on a (111) face at room temperature, i.e. about 296 K. The number of etch pits formed in this way is a measure for the dislocation content.

The sample surfaces were examined ex situ and in situ using bright field and differential interference contrast optical microscopy (DICM) and ex situ by AFM. For the ex situ AFM observations the side $\{111\}$ faces were used, because of the top (111) face showed a slight shut off effect, which masks the finest details that can be seen by this scanning probe method. The AFMs used, a Digital Dimension 3100 and a Digital Instruments Nanoscope III, were operated in contact mode. In the first case, both height and deflection (error-signal) images were recorded simultaneously, whereas for the second instrument only the deflection technique was used.

3. Observations

3.1. General

To obtain information about the influence of the concentration of the formamide in our growth solution on the stabilization of the $\{111\}$ faces of NaCl, we grew crystals from saturated water solutions without formamide, with formamide added in 10 and 25 wt.% and in pure formamide. In the first case, only the set of $\{100\}$ faces was obtained. This implies that the growth rate of the $\{111\}$ faces, $V_{\{111\}}$ is larger than $\sqrt{3}V_{\{100\}}$, where $V_{\{100\}}$ is

the growth rate of the cubic faces. In the second case two sets of faces appeared, namely $\{100\}$ and $\{111\}$, whereas in the third and the fourth case only octahedrons were formed. This means that, in the latter two cases the growth rate $V_{\{111\}}$, is smaller than $1/\sqrt{3}V_{\{100\}}$, which indicates a substantial change in relative growth rates. From these observations it is clear that, in contrast to growth from pure aqueous solutions, formamide stabilizes the octahedral faces with respect to the cubic faces. A similar observations have been reported earlier [13,17,18]. Relating the occurrence of cubo-octahedral forms at ~ 10 wt.% formamide concentration with the morphodrome obtained by Bienfait et al. [13], indicates that the relative supersaturation in our experiments is about 7%. It is interesting to note that the quality of the crystals grown from aqueous solution with formamide added was significantly better than those grown from pure aqueous solution. The number of liquid inclusions was reduced to a large extent. Using urea as impurity in the growth solution resulted in a similar stabilization of the $\{111\}$ faces as found for formamide. On the other hand, we did not observe the appearance of octahedral faces by adding dimethylformamide and benzamide as impurities in our NaCl–water growth solution.

3.2. Morphology of $\{111\}$ faces grown from water–formamide solutions

Fig. 1a represents an ex situ AFM image of a circular growth hillock observed on a (111) NaCl surface grown from a formamide–water solution. The radius of this hillock is ~ 30 μm , its height is ~ 70 nm. The steps of the hillock, which range in height from 3 to 11 nm, are much higher than monomolecular steps. We think that this is due to interaction of advancing steps with impurity molecules, which causes bunching in trains of steps [19]. It is suggested that the steps on the (111) surface are produced by a composite growth spiral originating from a bundle of screw dislocations, although it is difficult to prove this, because the central part could not be resolved by AFM. The type of hillock as shown in Fig. 1 was commonly found on the crystals grown from the supersaturated water–formamide solutions. Etching of the

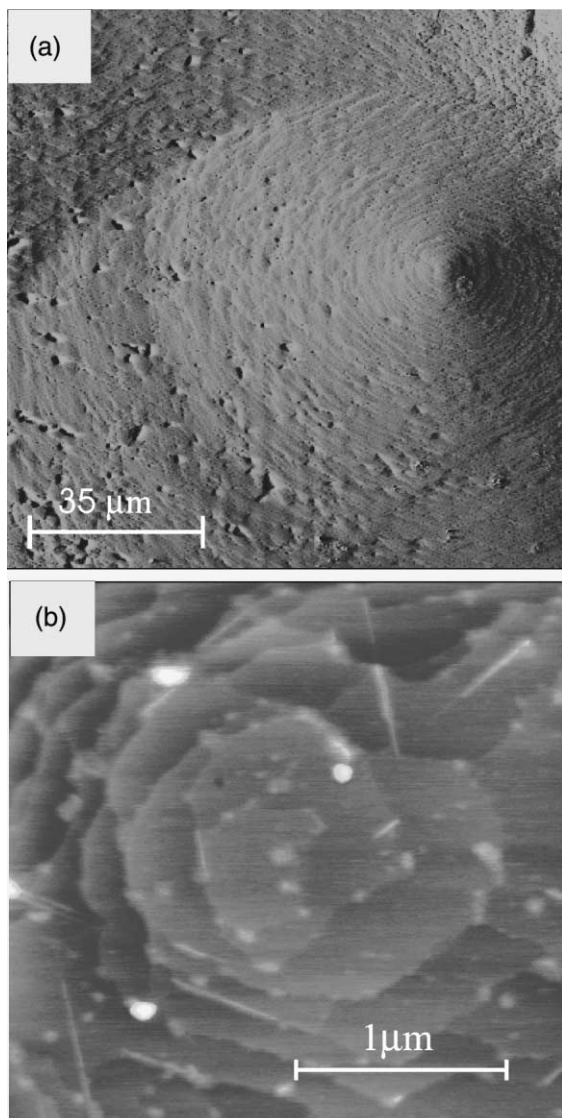


Fig. 1. Ex situ AFM images of growth spirals observed on $\{111\}$ NaCl crystal surfaces grown from aqueous NaCl solution with 25 wt.% of formamide added: (a) Typical growth hillock, presumably originating from a dislocation bundle. Its slope is about 0.25° ; the step height ranges from 3 to 11 nm; (b) Spiral with monomolecular steps of height $d_{\{111\}} = 0.3$ nm. One monomolecular step consists of one Na^+ layer and one Cl^- layer.

$\{111\}$ NaCl crystal surface in formamide produced a large number of etch pits $\sim 4 \times 10^4$ per mm^2 , which were persistent upon continued etching. This indicates that they are dislocation pits,

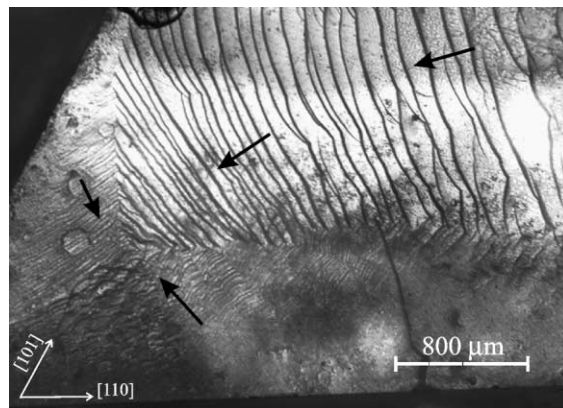


Fig. 2. Ex situ optical image of a typical $\{111\}$ NaCl crystal surface grown from a water–formamide solution. It can be noticed that the motion of the steps starts from the edges of the crystal and goes towards the central depression. The directions of step flow are indicated by arrows.

and shows that a large number of dislocations are available for the creation of the spirals. Beside the typical bunched spirals, a few growth spirals with monomolecular (0.3 nm in height) steps were also observed (Fig. 1b). The top of these spirals was easily resolved by AFM.

Fig. 2 represents an ex situ optical image of a typical $\{111\}$ NaCl crystal surface. On this picture it can be noticed that motion of the steps starts from the edges of the crystal, going towards the center of the surface. Such a pattern indicates the onset of hopper growth, where due to an enhanced supersaturation steps preferentially nucleate near the edges of the crystal surface. This step motion from the edges is very often influenced by and in competition with steps that originate from the spiral hillocks.

Apart from higher steps, also monomolecular steps with the lowest possible heights according to the interplanar distance were observed on the $\{111\}$ faces of NaCl (Fig. 3). These steps were found on almost all side $\{111\}$ faces of the crystals. AFM measurements proved the step height to be about 0.3 nm. This is in agreement with the interplanar distance, $d_{\{111\}}$, between adjacent $\{111\}$ planes, which is $(1/3)\sqrt{3}a = 0.325$ nm, with $a = 0.563$ nm as the cell parameter of the cubic unit cell. One monomolecular step consists of one Na^+ layer and one Cl^- layer.

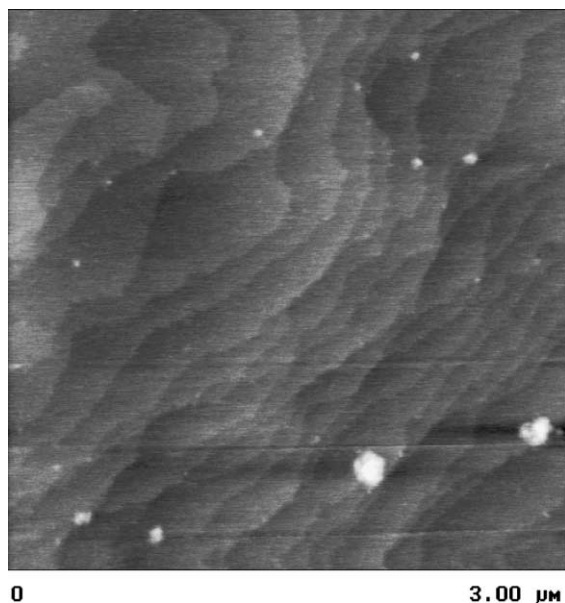


Fig. 3. AFM image showing monomolecular steps on a (111) NaCl crystal surface grown from an aqueous NaCl solution with 25 wt.% formamide. Step height is about 0.3 nm. Each monomolecular step consists of one Na^+ layer and one Cl^- layer.

Good atomic resolution is also achieved. The surfaces appear as presented in Fig. 4, in which oriented patterns of single bright spots, referring to the positions of single ionic species are visible. Arrangements with hexagonal symmetry are the only observed structure. The observed interatomic distances are 0.39 nm, which is in excellent agreement with the calculated distance between two adjacent ions of equal sign in the (111) plane (0.395 nm). This observation shows that the surface is not reconstructed. Confirmation is recently obtained by surface X-ray diffraction on {111} NaCl crystals prepared in the same way. This will be elaborated in a forthcoming paper.

3.3. Morphology of {111} faces grown from pure water solutions

After submerging the {111} faces into a supersaturated NaCl solution in pure water, a surface morphology is obtained which is different from that obtained from water–formamide solu-

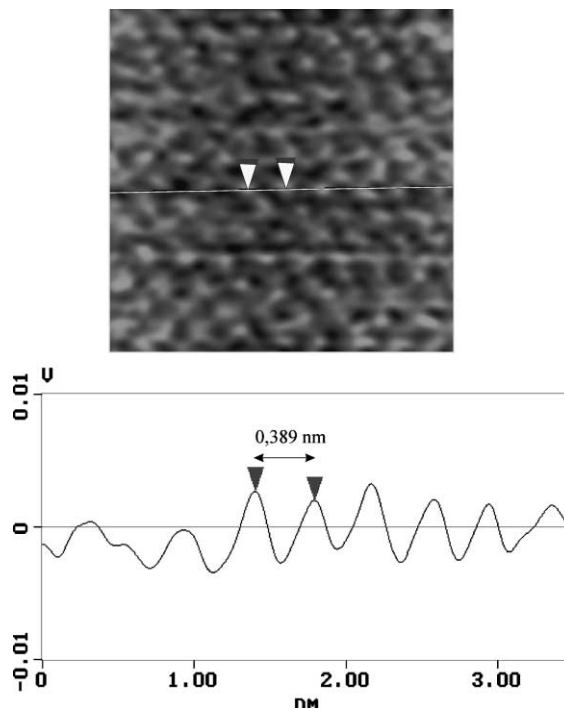


Fig. 4. AFM image with atomic resolution of a (111) NaCl surface grown from a water–formamide solution, in which the oriented patterns of the single bright spots refer to the positions of single ionic species. The observed interatomic distances are 0.39 nm.

tions. Now, shallow growth hillocks with rounded tops develop, which were also observed in situ using optical microscopy. Fig. 5 presents an optical as well as an AFM image of these protrusions. AFM observation of these hillocks showed islands of one or more unit cells high and about 150 nm wide, but no arrays of steps were observed.

After a longer period of {111} surface growth, a multitude of triangular growth pits, leading to a macroscopic roughness of the crystal surface, develop (Fig. 6). Careful measurement using optical microscopy shows that the side walls of the pits are inclined $36 \pm 2^\circ$ with respect to {111} in the zone $\langle -110 \rangle$, i.e. are $\sim \{114\}$ faces. As will be elaborated in the discussion section, this indicates that the {111} faces grow faster than {100} faces.

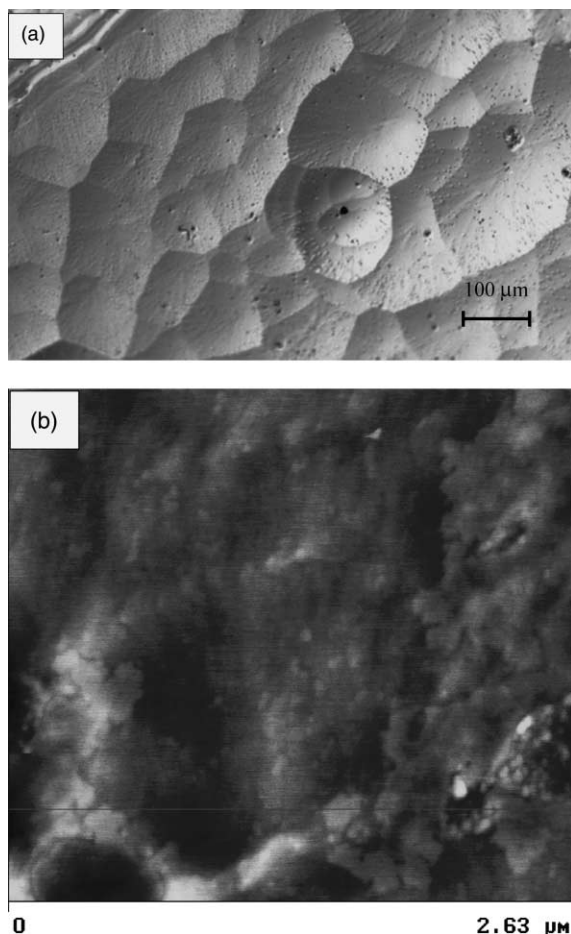


Fig. 5. Shallow growth hillocks obtained after covering a $\{111\}$ NaCl crystal surface with a droplet of a supersaturated NaCl solution in water: (a) optical differential interference contrast image recorded after 20 min of growth; (b) AFM image of these hillocks showing islands of one or more unit cells high. No arrays of steps were observed. Both images were mapped ex situ.

4. Discussion

4.1. Surface morphology of NaCl $\{111\}$ grown from water-formamide solutions

Observation by optical microscopy and AFM showed that growth of the $\{111\}$ faces proceeds by extended arrays of monomolecular and higher steps. This indicates that growth occurs far below the roughening temperature. The circular shape of

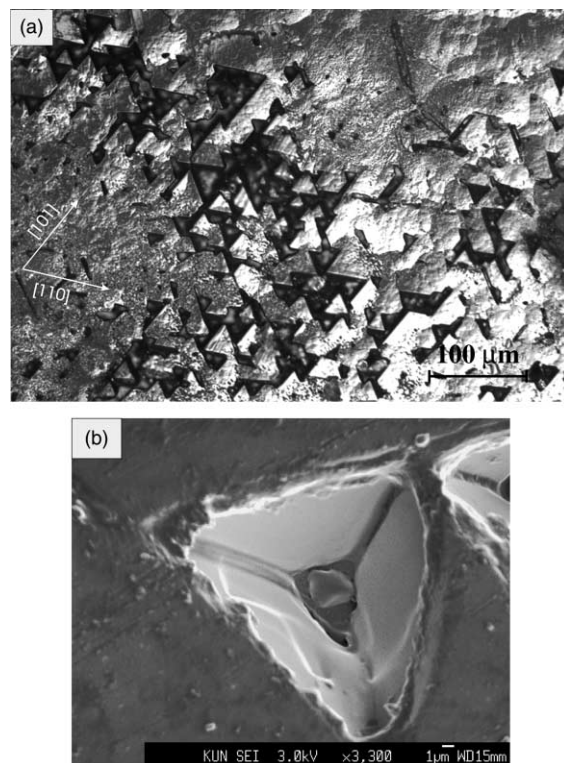


Fig. 6. A multitude of triangular growth pits develop after a longer period of $\{111\}$ NaCl surface growth from pure water solution. The side walls of the pits consist of $\sim\{114\}$ faces: (a) optical image giving overview; (b) scanning electron microscope image showing one pit in detail.

the hillocks and step patterns points to either growth limited by surface diffusion or to a low kink energy resulting in a high density of kinks at the steps [20]. Two mechanisms are responsible for the generation of the steps. The first mechanism is spiral growth due to the presence of screw dislocations, which are step sources allowing exactly oriented crystal facets to grow at low supersaturation. This leads to the development of spiral hillocks. In many cases we noticed a competition between different hillocks for being a dominant step source. The second mechanism is two-dimensional nucleation of steps starting from the edges of the crystal surface causing step motion towards its centre.

In the case of growth from water-formamide solutions it was found, using AFM, that no re-

construction occurs for the $\{111\}$ surfaces. This implies that, apart from possible relaxation, it looks like a truncated bulk phase. Here the dipole moment and electrostatic repulsive next-nearest-neighbour bond energies of the polar $\{111\}$ surface are obviously compensated by solute ions, as well as by formamide molecules and, to some extent, water molecules, which both have a dipole moment. It was also observed that the lowest steps are monomolecular, i.e. consist of one Na^+ and one Cl^- layer. Never $(1/2)d_{\{111\}}$ steps, either corresponding to one Na^+ layer or one Cl^- layer were found. This means that always one type of ion is on top of the $\{111\}$ surface. Based on a model for the electrostatics using Gasteiger atomic charges [21], see Fig. 7, we suggest that the Na^+ layer is on top of the surface. The positive charge of the sodium is stabilized more effectively by the formamide than the negative charge of the chloride, due to the fact that the negatively charged oxygen of the formamide molecule is more exposed than the buried (shielded) positive charges on the carbon atom. The NH_2 group is almost electrically neutral. Therefore, the oxygen can have a more direct interaction with neighbouring ions. The strong

interaction between Na^+ ions of the $\{111\}$ NaCl crystal face and electronegative O atoms of formamide results in a stabilizing adsorption of formamide on a $\{111\}$ face with the Na^+ ions on top of the Cl^- ions.

We observed that formamide and urea both stabilize the $\{111\}$ NaCl faces, whereas similar, but bigger molecules such as dimethylformamide and benzamide do not. Structure formulas of formamide, urea, dimethylformamide and benzamide are presented in Fig. 7. It can be noticed that all molecules have similar charge distribution, where the charge on the oxygen is more important than the shielded charges on the carbon atoms and the NH_2 group. Formamide, with molecular volume $V \approx 41 \text{ \AA}^3$ and urea with $V \approx 53 \text{ \AA}^3$ are smaller molecules as compared to dimethylformamide ($V \approx 75 \text{ \AA}^3$) and benzamide ($V \approx 113 \text{ \AA}^3$). Molecular volume is here defined as the volume inside the Van der Waals surface. From the above, it can be concluded that the smaller molecular volume and the preferential charging of the electronegative oxygen enable nice adsorption of formamide and urea on the $\{111\}$ NaCl surface and therefore stabilize that face. For the two homologous molecules with the same charge distribution but larger molecular volume, steric hindrance prevents this effect.

We also noticed that the quality of the crystals grown from aqueous solution with formamide added was significantly better than those grown from pure water solution. This can be explained by the fact that in the presence of formamide the crystals grow considerably slower than from pure aqueous solutions, which is a result of formamide molecule adsorption on the $\{111\}$ NaCl crystal surface. The slower growth reduces the extent of morphological instability caused by mass transport limited growth, and thus decreases the formation of liquid inclusions.

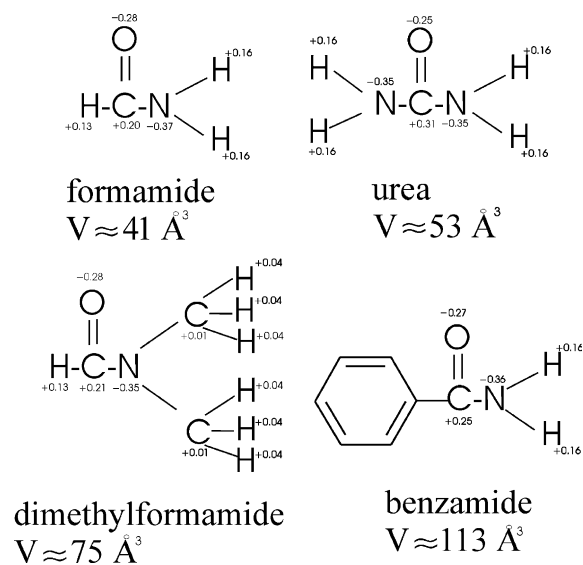


Fig. 7. Structure formulas and calculated charge distributions of homologous compounds used in our growth solution to determine their influence on the stabilization of $\{111\}$ NaCl faces.

4.2. Surface morphology NaCl $\{111\}$ grown from pure water solutions

4.2.1. Growth hillocks

In the case of growth of NaCl $\{111\}$ faces from supersaturated NaCl solutions in pure water, a surface morphology which is quite different from

that for growth from water–formamide solutions is obtained. We presume that the development of the shallow hillocks with rounded tops is related to dislocations and growth takes place close to the roughening temperature. Close examination of these hillocks using AFM revealed islands of one or several unit cells high. At the same time we observed no periodic steps patterns. Here 2D nucleation or even random deposition of growth units plays a main role. Monte Carlo simulations of the dislocation growth of a $\{100\}$ Kossel crystal surface near the kinetic roughening transition indeed show that growth hillocks without clear concentric steps patterns develop [22]. This explanation indicates that the $\{111\}$ surface grows close to its roughening transition. It causes fast growth and thus accounts for the absence of the $\{111\}$ faces on the morphology of NaCl grown from pure aqueous solutions.

4.2.2. Growth pits

After a longer period of $\{111\}$ NaCl surface growth, a multitude of growth pits, leading to a macroscopic roughness of the crystal surface develop. The side walls of the pits consist of approximately $\{114\}$ faces, which are $36 \pm 2^\circ$ oriented with respect to the $\{111\}$ growth face. Recently the concept of “velocity source” has been introduced and used to explain the occurrence of etch and growth pits, hillocks and other features on crystal surfaces [17,23,24]. A velocity source is a point or line on a crystal surface at which the growth/etch rate is locally different. As a consequence of this, the shape of the crystal surface adapts accordingly. In our case a masking particle, for instance a speckle of dust which locally retards growth, is the velocity source. It is situated at the bottom of the pit. The adaptation of the surface is growth pit formed.

The surface orientations around the velocity source, i.e. the side walls of the growth pits, must fulfil the connectivity relation [23,24]:

$$|\vec{R}_{\text{wall}}| = \vec{n}_{\text{wall}} \cdot \vec{R}_{\text{VS}}. \quad (1)$$

Here \vec{R}_{wall} is the growth rate of the growth pit walls, \vec{n}_{wall} the orientation of growth pit walls and \vec{R}_{VS} the growth velocity of the $\{111\}$ surface below the semipermeable mask (which is less than

$\vec{R}_{\{111\}}$). From the connectivity condition it follows that the particle must be *semipermeable*, i.e. $\vec{R}_{\text{VS}} \neq 0$, else Eq. (1) cannot be satisfied and no growth pit will be formed. A second consequence of the connectivity condition is the fact that on the slowest growing surface of a crystal no growth pits can be formed, because then $\vec{n}_{\text{wall}} \cdot \vec{R}_{\text{VS}}$ is always less than (and never equal to) the smallest possible \vec{R}_{wall} . Since $\{100\}$ is the slowest growing face of the NaCl crystal when crystallizing from a pure water solution, this explains why this surface never gives growth pits. However, it is shown here that using same solution, the $\{111\}$ faces grow much faster than $\{100\}$, so here the connectivity condition can be satisfied and pits are formed. The growth rate of the $\{100\}$ surfaces as a sidewall of the growth pits is too slow to satisfy Eq. (1). Therefore the pit wall adjusts itself to the faster growing orientations approximately $\{114\}$ to fulfil the connectivity condition.

The requirement that a pit expands during continued growing is also given in Ref. [25]:

$$\vec{R}_{\{111\}} \cdot \vec{n}_{\text{wall}} > |\vec{R}_{\text{wall}}|. \quad (2)$$

Because of the semipermeable property of the masking particle, $\vec{R}_{\text{VS}} < \vec{R}_{\{111\}}$, and from Eq. (1) it follows that condition (2) is always fulfilled.

According to our observations, the pits obtained during the growth of the $\{111\}$ NaCl from water solutions is the reversed case of the etch pyramids obtained after formamide etching of the $\{100\}$ NaCl crystal surface [17] or wet chemical etching of $\{100\}$ Si [23,24].

5. Conclusions

Octahedral NaCl single crystals of several millimeters to one centimeter in size with large, flat and stable $\{111\}$ faces can be obtained from solution. It was shown that aqueous solutions containing formamide and urea stabilize this NaCl form, whereas larger, homologous molecules, such as dimethylformamide and benzamide, do not.

AFM and optical microscopy showed that the growth of NaCl $\{111\}$ crystal faces from aqueous solutions containing formamide proceeds by monomolecular and higher layers, with most prob-

ably Na⁺ ions on top of Cl⁻ ions. Steps originate from spiral-dislocation growth as well as from 2D nucleation starting from the edges of the crystal. Atomic resolution imaging of NaCl {111} using AFM showed no surface reconstruction.

The morphology of the {111} faces grown from pure water solutions showed different surface patterns, i.e. shallow growth hillocks with a rounded top develop. We presume that that these hillocks are related to dislocations and growth proceeds close to the roughening temperature. Growth pits are formed after a longer period of {111} surface growth in pure water solution. These are produced by a mechanism which is similar, but opposite to that of the etch pyramids obtained after formamide etching of the {100} NaCl crystal surface [17].

Acknowledgements

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