

## Summary

When crystals are growing from a solution, the solid-liquid interface is the place where the crystal interacts with its environment and therefore the structure of this interface will control the growth process. In first instance the growth morphology is determined by the crystallographic structure of the crystals, but other important factors are impurities, solvents, temperature, supersaturation and surface relaxation. All systems investigated in this thesis are ionic crystals grown from aqueous solution. Unlike the situation for crystals with metallic, covalent or molecular bonding types, there are essentially no theoretical models that are sufficiently accurate to make general predictions on the behavior of surfaces of ionic crystals, neither in vacuum nor in an aqueous environment.

In chapters two and three the growth of cesium halides (CsCl, CsBr and CsI) from aqueous and formamide solutions is investigated. Equilibrium forms of the three cesium halides in aqueous solution are obtained at temperatures ranging from 275-344K. A first bond order connected net analysis predicts that below the roughening transition the equilibrium form of the three halides is dodecahedral, i.e, determined by  $\{110\}$  faces. This was indeed the morphology found for CsI over entire temperature range investigated. The CsCl crystals, on the other hand show rounded facets, which indicates they are above the roughening temperature. For CsBr, a roughening transition was observed at a temperature of  $278 \pm 1$  K, with a transition that is far more abrupt than the normal thermal roughening. As far

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as we know, this is the first time that a thermal roughening transition has been observed for a simple ionic compound.

In contrast to the predicted dodecahedral growth form, cesium halides can also crystallize in a cubic morphology, as described in chapter three. The metastable cubes transform after a period of seconds to minutes into rough, grainy cubes. The unstable cubes likely have the fcc rock salt structure. Stable cubes were only obtained by crystallizing cesium halides from pure, water-free formamide. These transparent cubes, bounded by  $\{100\}$  faces, have the primitive cubic cesium chloride structure, as was shown by single crystal X-ray diffraction. Atomic resolution images from atomic-force microscopy show that the surface is not reconstructed, as has been predicted by theory, but is directly stabilized by the polar formamide molecules.

A proper understanding of crystal growth from solution requires structural knowledge of the solid-liquid interface at the atomic scale. In chapter four we have determined the structure of the  $\{101\}$  face of ammonium di-hydrogen phosphate (ADP) in aqueous solution using surface X-ray diffraction. We find that a layer of ammonium ions terminates the  $\{101\}$  face, followed by a layer of phosphate ions. For a proper description of the experimental data, a 50% contraction of the top layer spacing needs to be included. The most striking difference with the isomorphous KDP crystal is the reversal of the direction of relaxation of the outmost layer. Hydrogen bonding in ADP is a likely cause for this difference.

In the last two chapters, liquid ordering at the brushite and NaCl/water interface is studied. Our data show that water in contact with the brushite  $\{010\}$  surface shows less ordering than “expected”, in particular when

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compared with the water ordering at the KDP{101}-water interface. Water in contact with the positively charged KDP {010} surface shows icelike ordering in the first two water layers and weak but clear in-plane ordering in the third water layer. For the brushite system that contains water layers in the crystal structure, less ordering is found. We propose that this difference is correlated with the large difference in solubility.

The atomic structure of the NaCl{100}/water interface was determined under four conditions of increasing humidity i.e, ultra high vacuum, dry nitrogen atmosphere, 45% and 75% relative humidity. Details of the atomic structure are determined on both sides of the solid-liquid interface. The top most layer of NaCl shows a small relaxation that changes from an expansion to a contraction with increasing humidity. Under all measured conditions, water monolayers with different ordering properties are present at the interface. At low humidity a diffuse water monolayer covers the NaCl surface, showing only a weak lateral ordering induced by the NaCl surface. Surprisingly, at relative humidities above 45% the first water monolayer *increases* its lateral ordering. Subsequent layers rapidly evolve towards bulk like water. The relative strong ordering at the NaCl surface is in agreement with our hypothesis that the level of water ordering at the interface is correlated with the solubility of the compound in water.

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