The structure at a solid-liquid interface determines many important processes, such as crystal growth, wetting, lubrication, and catalysis. Also from a fundamental point of view, the ordering of a liquid in contact with a solid is of interest. In recent years several predictions from theoretical models and computer simulations have been verified using x-ray diffraction (XRD). The ordering in the perpendicular direction ("layering") is found to be stronger than in the lateral direction, and extends typically over three to five monolayers. The lateral ordering has only recently been determined for a few systems.

Now that the global properties of solid-liquid interfaces have been confirmed, it is important to investigate the role of the solid-liquid interface in actual processes. Here we focus on crystal growth from solution, in which case the solvent is often found to determine the morphology of the crystal or the particular polymorphic form that is grown. The crystal investigated here is potassium-dihydrogen-phosphate (KDP, KH₂PO₄), whose morphology depends on the pH of the aqueous growth solution. The growth morphology is determined by the {100} and {101} faces, where the growth velocity of the {101} face shows a quite strong dependence on the pH and is maximal for a stoichiometric solution.

The structure at a solid-liquid interface determines many important processes, such as crystal growth, wetting, lubrication, and catalysis. Also from a fundamental point of view, the ordering of a liquid in contact with a solid is of interest. In recent years several predictions from theoretical models and computer simulations have been verified using x-ray diffraction (XRD). The ordering in the perpendicular direction (“layering”) is found to be stronger than in the lateral direction, and extends typically over three to five monolayers. The lateral ordering has only recently been determined for a few systems.

Now that the global properties of solid-liquid interfaces have been confirmed, it is important to investigate the role of the solid-liquid interface in actual processes. Here we focus on crystal growth from solution, in which case the solvent is often found to determine the morphology of the crystal or the particular polymorphic form that is grown. The crystal investigated here is potassium-dihydrogen-phosphate (KDP, KH₂PO₄), whose morphology depends on the pH of the aqueous growth solution. The growth morphology is determined by the {100} and {101} faces, where the growth velocity of the {101} face shows a quite strong dependence on the pH and is maximal for a stoichiometric solution (pH=4). The situation for the {100} face is less clear, which could be due to the high sensitivity of that face to impurities.

For stoichiometric conditions the surface structure of the {100} and the {101} crystal face has been determined, and for the {101} face in addition the interfacial liquid was found to show icelike ordering. Here we report the solid-liquid interfacial structure of the {100} and {101} faces for three different pH values as determined using surface XRD. We find a remarkable large change for the {101} face, while the {100} face is hardly affected. We find evidence for ordering in the liquid, not only of the solvent but also of the solute molecules/ions. This is the first time that changes in the crystal growth morphology have been correlated with changes in the structure at a solid-liquid interface.

Surface XRD is very suitable for determining the atomic structure at the interface of a crystal surface with a solution, because of the large penetration depth of X rays. The interface structure can be derived from structure factors measured along the so-called crystal truncation rods. These rods originate from the interference sum between bulk and surface signals of the crystal and include contributions from the ordered liquid at the interface. By including rods with different values for the in-plane momentum transfer, sensitivity to both the laterally ordered and disordered parts of the solid-liquid interface is achieved. The experiments were performed at the DUBBLE beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, using an X-ray energy of 16 keV. The setup consists of a growth chamber coupled to a (2+3) diffractometer operating in a vertical geometry. In order to increase the accessible range along a rod, data were collected with incoming angles 1° and 15°. A KDP crystal with a size of 3–6 mm was immersed in a saturated solution with specific pH; for each pH a new crystal was prepared. By adding H₃PO₄ or KOH, pH values of 3 or 6, respectively, were obtained.

To describe the surface unit cell of the {101} KDP crystal the following lattice vectors are introduced:

\[ a_1 = \frac{1}{2} [111]_{\text{tetragonal}}, \quad a_2 = \frac{1}{2} [111]_{\text{tetragonal}}, \]

\[ a_3 = \frac{1}{2} [010]_{\text{tetragonal}}. \]

The corresponding reciprocal lattice vectors \( b_i \) are defined by \( a_i \cdot b_j = 2\pi \delta_{ij} \). The momentum transfer vector is then denoted by \( Q = h b_1 + k b_2 + l b_3 \) with (hkl) the diffraction indices. The index \( l \) is the direction perpendicular to the surface, each rod is labeled by indices (hk).

We collected data sets for pH=3, pH=4.4, and pH=6 for both the {101} and the {100} face. Each data set of the {101} face consists of the (00), (10), (01) and (20) rods, with a total of 250 reflections. The P₁ symmetry of the {101} surface means that equivalent reflections are absent. However, the reproducibility for different incoming angles for the same reflection is 8%. The measured intensities were converted into structure factors by applying a standard procedure. The parameters describing our models were fitted to experimental structure factors using a least-squares method employing the ROD surface crystallographic software.

Figure 1 shows part of the data measured on the {101} face. There is a remarkably large difference between the three pH values, therefore the interface structure depends strongly on the pH of the solution. In contrast to this, the data acquired from the prismatic {100} face are the same for

```
1098-0121/2005/72(24)/245404(5)/$23.00 245404-1 ©2005 The American Physical Society
```
curves represent the best fit models for the measured data and for a
inverting the structure factors according to Friedel’s rule. The
of water molecules and the various ions from KDP
plane ordering were modeled by giving these a very large
interfacial liquid layers is modeled using
interface is modeled. The different degrees of ordering of the
data using models that describe both sides of the solid-liquid
therefore conclude that for this face the structure is the same
all pH values within the estimated accuracy (not shown). We
In order to determine the interface structures, we fitted the
data using models that describe both sides of the solid-liquid interface, as shown schematically in Fig. 2. For the crystal-
line part, the occupancy and position of the atoms near the
The solution consists of water molecules and the various ions from KDP
the data are only moderately sensitive to the atom
type. We can therefore initially model the liquid by using
only layers of oxygen atoms (ignoring the hydrogen in the
water for which the x rays are insensitive). If the occupancy of these oxygen atoms (labeled O1, O2, etc.) is found to be
higher than 1, this is an indication that the corresponding
layer contains heavier atoms. We found that surface rough-
ness is negligible.
Since there is no significant variation in the data as a
function of the pH value for the (100) face, we mention the
fit results here only briefly; a more extensive discussion will
be given elsewhere. In agreement with earlier results, we
find that the crystal is bulk terminated with negligible relax-
ation. The more precise data obtained here further show that
the formation of an H bond between crystal and solution is
the most important structural feature. This bond will not be
affected by the pH value, explaining the constant structure of the
interface.
For the (101) face we start our discussion with pH=4.4,
the stoichiometric value for which the full interface structure
was determined earlier by Reedijk et al. using a water film
with a thickness of only 22 Å. We obtain essentially the
same results, thus a thin film can be representative of a solid-
liquid interface. The topmost K⁺ and H₂PO₄⁻ layers show
small relaxations, and there are four water layers visible of
which the first two are highly ordered (“icelike”). There are
only differences in the lateral position of layers O1 and O2
and the occupancy of O1. In the present analysis we find two
similar minima in the least-squares optimization, one of
which is the same as that reported by Reedijk et al., but
another one yields an O2 position in which the distance to the
K⁺-ion is a more realistic 2.38 Å (compared to 1.97 Å).
Table I shows the optimum parameters together with the ear-
lier results, and Fig. 1 shows the best fit. The position of O1
is near the extrapolated lattice position of a next K⁺ ion,
suggesting that this layer partly consists of K⁺ ions instead of
water molecules. The occupancy, however, is only 0.63 assum-
ing water at this location, so that the fraction of K is 0.3 at
most.
For pH=6 we start the fit using the same model, but we
find that in this case a high electron density in the first liquid
layer is required in order to obtain a good fit. Now the position
(in fractional coordinates) of O1 of (0.84, 0.15, 1.37) is
even closer to the extrapolated position of a bulk K⁺ ion of
(0.875, 0.125, 1.375) and the occupancy for O1 is larger than 1.
Replacing the O atom by a K⁺ ion, we get essentially the
same fit with a K occupancy of 0.56, making it likely that a
substantial part of this site is occupied by K⁺ ions. Other
significant differences with pH=4.4 are a much lower order
in layer O2 and a lower perpendicular order in O3. The fit
results are shown in Fig. 1 and in Table I.
For pH=3 a low electron density in the first layer is re-
quired to obtain a good fit and the lateral position differs
from that expected for K⁺, thus ruling out a significant K⁺
concentration at this location (<15%). The order in layers
O2 and O3, by contrast, is increasing. This occurs at a height
corresponding to the bulk-extrapolated position of
H₂PO₄⁻. Together with the relatively high occupancy value in layer O2, this suggests that layers O2 and O3 contain a high concentration of H₂PO₄⁻. The lateral order in
these layers is much less than in layer O1, as expected from

FIG. 1. Measured structure factors (symbols) along the (00) and
(01) rods of the {101} face. The negative / values are obtained by
inverting the structure factors according to Friedel’s rule. The
curves represent the best fit models for the measured data and for a
bulk-terminated crystal.

FIG. 2. The schematic structure at a solid liquid interface at
which the liquid is evolving towards a bulk liquid over a few layers.
The partial order in the layers closest to the crystal surface is mod-
eled using anisotropic Debye-Waller parameters.
TABLE I. Best fit parameters for the \{101\} face. All positions \((x, y, z)\) are expressed as fractions of the unit cell parameters, except \(\Delta z\) which is in Å with respect to an unrelaxed bulk position. Values with asterisks are fixed. The layers O1-O4 represent water layers, but two alternative fits are listed as well: in layers O2-O3 at pH=3 a fit assuming P layers and in layer O1 at pH=6 a fit with a K layer. In both cases, mainly the occupancy value is changed. The origin is chosen such that K has unrelaxed coordinates \((0.75, 0.25, 1.25)\).

<table>
<thead>
<tr>
<th>Layer</th>
<th>Par.</th>
<th>pH=3</th>
<th>pH=4.4</th>
<th>pH=6</th>
<th>Ref. 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>O4</td>
<td>(z)</td>
<td>1.63(8)</td>
<td>1.61(8)</td>
<td>1.67(6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_\parallel [\text{Å}^2])</td>
<td>1000*</td>
<td>1000*</td>
<td>1000*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B_\perp [\text{Å}^2])</td>
<td>470(240)</td>
<td>505(100)</td>
<td>283(104)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Occ.</td>
<td>7(4)</td>
<td>5(4)</td>
<td>5(3)</td>
<td></td>
</tr>
<tr>
<td>O3/P</td>
<td>(x)</td>
<td>0.51(2)</td>
<td>0.48(2)</td>
<td>0.43(2)</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>0.32(5)</td>
<td>0.41(3)</td>
<td>0.05(3)</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>1.50(1)</td>
<td>1.54(1)</td>
<td>1.52(2)</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>(B_\parallel [\text{Å}^2])</td>
<td>49(4)</td>
<td>35(4)</td>
<td>26(9)</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>(B_\perp [\text{Å}^2])</td>
<td>12(6)</td>
<td>18(5)</td>
<td>39(30)</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>Occ.</td>
<td>1.0(2)/0.55(3)</td>
<td>1.0(2)</td>
<td>2(1)</td>
<td>0.7</td>
</tr>
<tr>
<td>O2/P</td>
<td>(x)</td>
<td>0.02(1)</td>
<td>0.00(1)</td>
<td>0.06(2)</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>0.87(9)</td>
<td>0.86(4)</td>
<td>0.63(5)</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>1.46(1)</td>
<td>1.46(1)</td>
<td>1.43(2)</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>(B [\text{Å}^2])</td>
<td>22(8)</td>
<td>21(7)</td>
<td>197(20)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Occ.</td>
<td>1.7(4)/0.9(3)</td>
<td>1.5(3)</td>
<td>1.0(2)</td>
<td>1.4</td>
</tr>
<tr>
<td>O1/K</td>
<td>(x)</td>
<td>0.88(2)</td>
<td>0.86(2)</td>
<td>0.84(3)</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>0.32(9)</td>
<td>0.23(3)</td>
<td>0.15(2)</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>1.36(1)</td>
<td>1.37(1)</td>
<td>1.37(1)</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>(B [\text{Å}^2])</td>
<td>1.16*</td>
<td>1.16*</td>
<td>1.16^<em>/1.4^</em></td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Occ.</td>
<td>0.38(6)</td>
<td>0.63(6)</td>
<td>1.34(8)/0.56(3)</td>
<td>2.1</td>
</tr>
<tr>
<td>K</td>
<td>(\Delta z [\text{Å}])</td>
<td>0.10(4)</td>
<td>0.06(9)</td>
<td>-0.04(4)</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>1.260(4)</td>
<td>1.256(9)</td>
<td>1.246(4)</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>(B [\text{Å}^2])</td>
<td>1.4*</td>
<td>1.4*</td>
<td>1.4*</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Occ.</td>
<td>0.74(3)</td>
<td>0.85(3)</td>
<td>0.71(3)</td>
<td>0.69</td>
</tr>
<tr>
<td>PO_4</td>
<td>(\Delta z [\text{Å}])</td>
<td>0.00(2)</td>
<td>0.02(2)</td>
<td>0.04(2)</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>1.125(2)</td>
<td>1.127(2)</td>
<td>1.129(2)</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>Occ.</td>
<td>0.93(2)</td>
<td>0.96(2)</td>
<td>0.86(3)</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>(B_\parallel [\text{Å}^2])</td>
<td>0.85*</td>
<td>0.85*</td>
<td>0.85*</td>
<td>0.85*</td>
</tr>
<tr>
<td></td>
<td>(B_\perp [\text{Å}^2])</td>
<td>1.16*</td>
<td>1.16*</td>
<td>1.16*</td>
<td>1.16*</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td></td>
<td>2.66/2.67</td>
<td>2.68</td>
<td>2.69/2.50</td>
<td></td>
</tr>
</tbody>
</table>
layer, so it is likely that a significant fraction of this layer is occupied by O atoms (e.g., in the form of H$_3$O$^+$ ions). This agrees with the “icelike” layers reported at this pH.$^7$ At pH=3 this layer has largely disappeared.

How can we understand this behavior of the first liquid layer? One can start from two different points of view: electrochemical or crystallographic. The KDP[101] crystal terminates in a K$^+$ layer, thus from an electrochemical point of view the first liquid layer is expected to contain negative ions. This, however, has only limited validity because there is no net surface charge: the topmost K$^+$ layer is followed by two H$_2$PO$_4^-$ layers and another K$^+$ layer. The potential experienced by the solution is therefore much weaker than in the case of a genuinely charged layer and no normal electrochemical double layer is expected. The crystallographic point of view leads to a different conclusion. In the bulk of the crystal, the K$^+$ layer is followed by a second K$^+$ layer, and one would thus expect such a positive layer to be formed in the solution as well. The clearest experimental result is for pH=6, and this strongly points to a K$^+$ layer in the solution. In this case the crystallographic point of view appears to be valid, and the data show in fact crystalline preordering in the solution. Such an arrangement with two positive layers is unexpected from the electrochemical point of view, but is of course possible due to the lateral crystallographic structure of the system. The extra, partial K$^+$ layer leads to a net charge, which should be compensated by negative ions (H$_2$PO$_4^-$) as indeed indicated by the high occupancy in layers 2 and 3.

The next question is, why does this K$^+$-layer only occur at pH=6? This pH value is obtained by adding KOH to the growth solution, but the moderate increase in K$^+$ concentration ($\sim$10%) seems too small to account for the large change in the K density in the first liquid layer. If we maintain the crystallographic point of view that this layer should

![FIG. 3. A schematic of the interface structure of the {101} face (right) together with the $z$-projected electron density distribution (left) for the three pH values. The solid curves denote the layers with perpendicular order, the dashed curves show the density of layers with lateral order corresponding to the (10) rod.](image)
be positive, then the K⁺ ions may be replaced by other positive ions. The best candidates for these are the H₂O⁺ ions, the concentration of which increases by a factor 1000 going from pH=6 to pH=3. Their concentration remains much lower than that of the K⁺ ions, but H₂O⁺ has the advantage that it can form additional H bonds near the interface (e.g., to the topmost PO₄ groups in the crystal) and therefore be more favorable than K⁺ in this position. We thus propose that the competition between the chemisorption of K⁺ and H₂O⁺ explains the observed pH dependence. To fully understand this behavior, one has to know the solution chemistry of this system²² at the crystalline interface as a function of the pH value.

A second striking feature in the interface structure is the increasing lateral order in layer O₂ (at a z position near 10 Å) for decreasing pH values. This layer (and O₃) contains H₃PO₄⁻(3-x) ions, as derived from the position, the occupancy and from charge neutrality. If we assume that for decreasing pH the K⁺ ions in the first liquid layer are indeed replaced by H₂O⁺ ions, the increased lateral order can be due to the directional nature of the H bonds between H₂O⁺ and H₃PO₄⁻(3-x).

The structural differences are expected lead to changes in growth rate of the {101} face, because the incorporation of ions during growth involves several kinetic barriers²³ that will change with the interface structure. In addition, surface diffusion will be affected by the structural changes.²⁴ However, the present data do not directly reveal this relation between structure and growth velocity. In fact, the structural changes are found to vary monotonically, while the growth velocity is changing nonmonotonically and has a maximum for the middle pH value. Understanding this fully requires detailed modeling of the growth process based on the structural information derived here. Unfortunately, at present no such modeling software is available. The fact that on the {100} face the changes in the interface structure are minimal agrees with the minimal changes in growth velocity as a function of pH for that face.

In summary, we have shown that it is possible to observe the subtle structural changes that occur at the solid-liquid interface of a crystal as a function of the solution composition by using XRD and a high-quality crystal. The large changes at the {101} face and the absence of such changes at the {100} face as a function of pH correlate with the fact that the changes in the macroscopic growth velocity are large for the {101} and small for the {100} face. We find that chemisorption of solution ions occurs for both the {101} and {100} faces. These observations provide a good (but challenging!) starting point for a theoretical modeling of such interfaces in which the solution chemistry is taken into account.

We thank the DUBBLE staff for kind assistance during the experiment, J. J. De Yoreo for providing KDP crystals and Y. S. Wang for stimulating discussions. This work was made possible by financial support from the Council for Chemical Science of the Netherlands Organization for Scientific Research (CW-NWO).

---

21. A calculation shows that phosphate ions with random orientation give nearly the same intensity as a single phosphor atom.