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<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>M.F. Reedijk*, J. Arsic*, F.F.A. Hollander* and E. Vlieg*</b>  RIM dept. of Solid State Chemistry, University of Nijmegen, 6525 ED Nijmegen, The Netherlands		

## Report:

This experiment is part of a series of experiments on  $\text{KH}_2\text{PO}_4$  (KDP)-crystals, where we have tried to determine the atomic structure of a KDP-water interface. Here we focussed on the {101} face of the KDP crystals, which is composed of alternating layers of potassium ions and phosphate ions. The atomic structure of the crystalline part of the interface has been determined in the first experiments by de Vries et. al.<sup>1</sup>. They determined the structure of a KDP crystal in contact with a water layer of several micrometer thickness. The structure of the liquid side of the interface could not be determined in that experiment, because the background scattering of the bulk liquid was too high.

The aim of the present experiment was to determine the structure and ordering of the near-surface solution. This type of ordering is important for the stability of the faces and for understanding the growth behavior of crystals from solution. To investigate the structure of the liquid an ultra-thin water layer was needed to suppress the background scattering from the bulk liquid. Therefore we used a special 'humid' cell in which the relative humidity (RH) is 100% and the temperature can be controlled. In such conditions the crystal is covered with an ultra thin water layer.

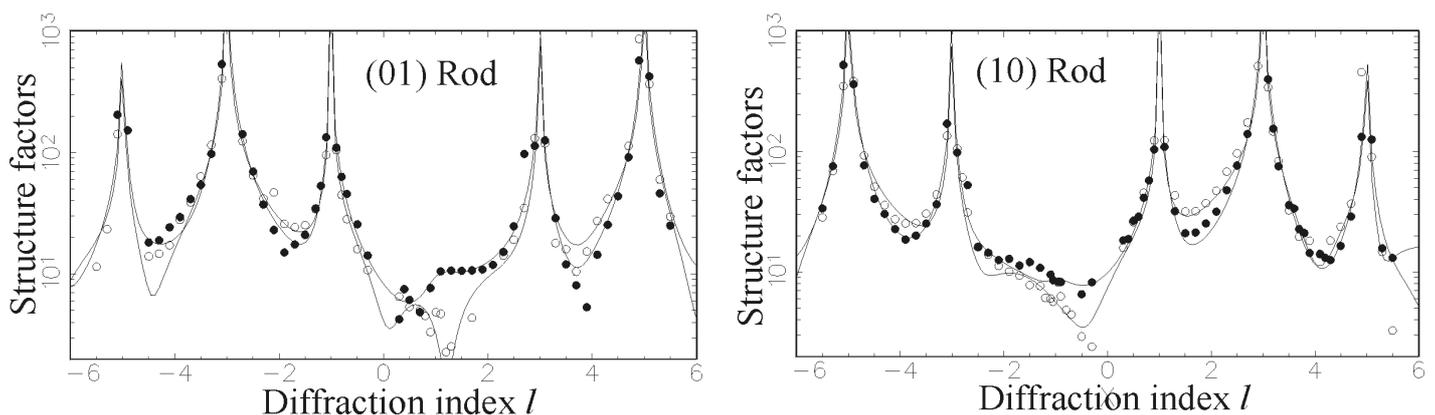
Experiments were performed in this 'humid' cell at room temperature, 45°C and 55°C. In addition, experiments were performed in a dry nitrogen flow and in air. In dry nitrogen no water is present, at 100% RH and 45°C approximately 20Å water is present. Complete data sets were measured including crystal truncation rods (CTRs), in-plane data and specular data at all five conditions. Both the crystal truncation rods and the in-plane data are sensitive to the in-plane ordering of the liquid. The specular data are sensitive to the electron density perpendicular to the surface.

Previous experiments, performed at ID32, already showed that the specular data measured in dry nitrogen differs from the specular data measured at 100% RH. These data

could only be fitted if layering of the solution near the interface was included. In addition, the present experiment shows that the structure of the liquid not only contributes to the specular data but also to crystal truncation rods with an in-plane momentum transfer, see figure 1. This indicates that the liquid layer has ordering perpendicular to the surface as well as parallel to the surface. This in-plane ordering extends over the first two water layers.

The complete data sets (including the specular data) were fitted starting with a potassium terminated surface, relaxations of the outermost potassium and phosphate groups were allowed. This is similar to the model used by de Vries et. al.<sup>1</sup>. In addition to this model, we find that part of the next potassium growth layer is already incorporated in the crystal. This was not observed at crystals covered with a water layer of several micrometer thickness. The saturated water layer is also included in the fit. To obtain a good agreement with the measured structure factors, ordering of the water layer has to be included. The first layer of water molecules is bound to the KDP surface, the position of this molecule is similar in all data sets. This layer has strong in-plane order. The subsequent water layer still shows some in-plane ordering which is vanished in the third water layer. All data sets at 100% RH show a similar behavior, although the details differ.

Thus, this experiment shows that the saturated solution in contact with the {101} face of KDP has both perpendicular and parallel ordering. The parallel ordering extends over two water layers.



**Figure 1**, The (01) and (10) crystal truncation rods, filled circles are data measured in nitrogen, open circles are data measured at 100% RH. The solid curves are the best fits.

<sup>1</sup>S. A. de Vries et al., *Phys. Rev. Letters* **80**, 2229 (1998).