



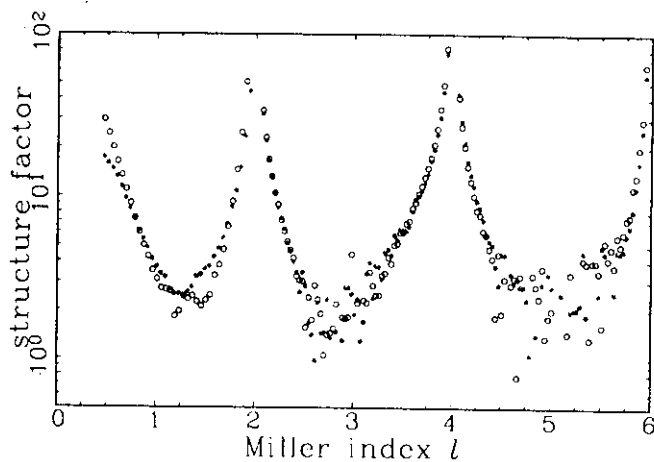
	Experiment title: Liquid structure at the KDP-water interface	Experiment number: SI-468
Beamline: ID32	Date of experiment: from: 15-2-1999 to: 23-2-1999	Date of report: 26-2-1999
Shifts: 24	Local contact(s): Luc Ortega	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): M.F. Reedijk ^{*1} , J. Arsic ^{*1} , S.A. de Vries ^{*2} , M. McBride ^{*3} and E. Vlieg ^{*1} ¹ <i>RIM dept. of Solid State Chemistry, University of Nijmegen, The Netherlands</i> ² <i>FOM-institute AMOLF, Amsterdam, The Netherlands</i> ³ <i>Lawrence Livermore Laboratories, Berkeley, CA, USA</i>		

Report:

The aim of the experiment was to find ordering of the solution in contact with the (101) and (100) faces of KDP. This type of ordering is important for the stability of the faces and for understanding the growth behaviour of crystals from solution.

The ordering of the liquid is expected to be very weak, and the strongest will occur in the direction perpendicular to the surface. These should thus be least difficult to observe in the specular reflectivity curve. In our earlier structure determination of the two faces [1], we used an environmental set-up in which such measurements were very difficult because of background problems. However, we have since learned that KDP surfaces are covered by a ultra-thin liquid layer when the humidity is high enough. This allowed us this run to accurately measure the specular reflectivity for both the (101) and the (100) faces. The figure shows results for the (101) surface. We have not yet had time to investigate the experimental results in any detail (the experiments stopped only a few days ago), but some initial conclusions can already be drawn.

We explored a simple way to see the effect of the liquid on the specular curve. By applying a flow of dry nitrogen gas, the liquid layer can be removed and a 'dry' specular curve can be measured. This can directly be compared with the 'wet' specular curve. An important lesson from our experiment is that the dry specular curve strongly depends on the conditions under which the surface is dried. The reason for this is as follows. At room temperature, a saturated aqueous solution contains about 20% KDP. When the water is quickly removed, the KDP will be randomly deposited and roughen the surface. We found



Specular reflectivity curve of KDP(101) as a function of perpendicular momentum transfer (in units of the Miller index l) for both a dry crystal (open circles) and a wet crystal (solid circles). The specular intensity has been converted to structure factor amplitudes. The deviation at lower l -values is due to the liquid structure at the interface.

that we could reproducibly smooth and roughen the surface on an atomic scale in this fashion. Only when the drying is very slow, the KDP growth units will have time to attach themselves at step sites without causing the roughness. We will check these observations by performing AFM experiments in the near future in our laboratory. The figure shows a dry specular curve that was obtained with very slow drying (open circles). The data at high values for the perpendicular momentum transfer (high Miller index l) coincide with that of wet KDP, which indicates that there is at least no crystalline, atomic-scale roughness. At l -values between 0 and 2 the curves show clear deviations, which therefore indicate the effect of the liquid on the interface structure. A more detailed analysis will tell us what the actual structure at this interface is.

Comparing wet specular curves with a set of wet crystal truncation rods (CTR's) (with in-plane momentum transfer) also gives information on the liquid ordering. The CTR's should be less sensitive to the liquid, because the in-plane ordering is expected to be less than along the specular direction. However, we were not able to collect a sufficiently accurate CTR data set, because the (101) crystals we used turned out to have an orientation that was 2° off from the crystallographic direction. These crystals were from the same batch of naturally grown faces that we used before [1] and for which no such problems were present. The same problem also severely hampered the accuracy (because of variations in the intensity in background scattering) with which radial scans could be performed. These scans in principle directly probe the pair-correlation function in the liquid.

The main experimental results therefore consist of sets of specular reflectivity curves on both (101) and (100) faces, obtained at various conditions (wet, dry, wet at higher temperature or humidity) and after various preparation methods of the crystal (etching, equilibration in a growth solution). The wet results turned out to be reproducible under various circumstances and should thus be a reliable start for a careful data analysis which is currently in progress. The diffractometer at ID32 (which had a special goniometer head) and the beamline optics performed very well during this run.

[1] S.A. de Vries et al, Phys. Rev. Lett. 80 (1998) 2229.