

Experiment title: INTERFACE STRUCTURE OF
KDP(101) AND KDP(100) IN SOLUTION *

**Experiment
number:**

SI 212

Beamline:

ID10

Date of Experiment:

from: November 14 to: November 22, 1996

Date of Report:

February 26, 1997

Shifts:

18

Local contact(s):

D.-M. Smilgies

Received at ESRF:

28 FEB. 1997

Names and affiliations of applicants (*indicates experimentalists):

S.A. de Vries*, P. Goettkindt*, and E.Vlieg*

FOM-Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands

D.-M. Smilgies*

European Synchrotron Radiation Facility, Grenoble, France

Report :

Recently it has become clear that in crystal growth from solution the interfacial region plays a much more important role than originally thought [1]. Both the liquid and the solid part of the interface are important, but as a first step we want to study the crystal structure. Potassium dihydrogen phosphate (KDP, KH_2PO_4) has a high crystal quality (no mosaic spread) and is a very interesting crystal both from a technological and a fundamental point of view. It is for example used as a frequency doubler and optical switch in laser applications. Theoretical studies correctly predict that the pyramid faces (101) and the prism faces $\{100\}$ are flat in solution, but for the (101) faces there are two possible terminations, either with PO_4^{3-} or K^+ ions. Knowing the detailed interface structure would help in understanding why impurities like Fe^{3+} and Cr^{3+} strongly reduce the growth velocity on the prism faces and have a much smaller effect on the pyramid faces [2].

We have studied the surface structure of both faces *in situ* using surface X-ray diffraction. The crystals were mounted in a growth chamber made of polycarbonate (LEXAN), consisting of an outer heating bath kept at a constant temperature by a thermostat. In the inner chamber the crystal is mounted in an environment of saturated KDP-solution. The incoming and outgoing X-rays penetrate through a thin mylar foil (6 μm) which can be pushed close to the crystal, leaving a thin layer of solution between the crystal and the foil (thickness $\sim 10 \mu\text{m}$).

On both the (101) and (100) surface we have measured the intensity along so-called crystal truncation rods (CTR's). These CTR's are tails of diffuse intensity connecting the bulk Bragg peaks in the direction perpendicular to the surface and show the interference between bulk and surface structure. The crystals are sufficiently flat to measure the CTR intensity far from the Bragg peaks, where the surface sensitivity is highest. For the X-ray wavelength used (0.73 Å), there is a lot of background

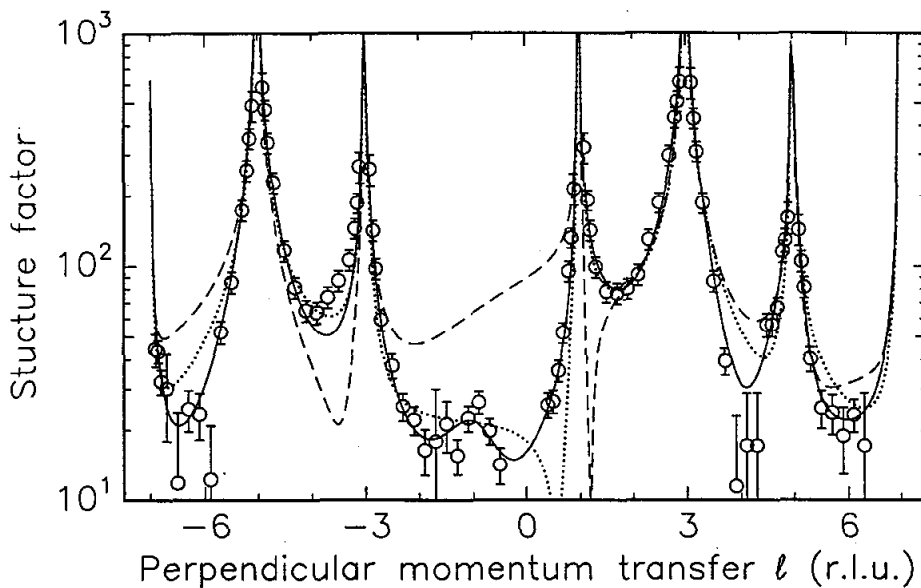


Figure 1. Structure factors along the $(hk) = (10)$ CTR for KDP(101). The dashed line is a calculation for a bulk K-terminated surface, the dotted curve for a PO_4 -terminated one. The solid line gives the best fit.

scattering from the crystal, but for larger wavelengths the attenuation in the solution becomes too high.

Figure 1 shows structure factor amplitudes along the $(hk) = (10)$ CTR measured on KDP(101) [3]. The dashed curve is a calculation for a bulk K-terminated surface and the dotted curve a calculation for a surface terminating with PO_4 . It is immediately clear that the surface is K-terminated. Allowing small relaxations of the top layer results in the solid line (which is a fit for the complete data set including the (11) and (2 1) CTR's). The structure determination was done at a temperature of 22 °C. While cooling to 21 °C, which corresponds to a supersaturation $\sigma = 2\%$, we monitored the (2 10.7) reflection. On growing the peak significantly sharpened which means the surface quality gets better. Heating up again (dissolution) causes a broadening of the peak shape.

On the (100) face also different CTR's were measured besides the specular reflectivity. From the CTR's we can conclude that this surface structure is simply bulk terminated. Further analysis of the data is currently in progress.

[1] X.Y. Liu, ES. Boek, W.J. Briels, and P. Bennema, Nature 374 (1995) 342.

[2] P. Bennema, "Growth and morphology of crystals", chapt. 7 in "Handbook of crystal growth", Vol. 1a (North Holland, Amsterdam, 1993).

[3] S.A. de Vries, P. Goettkindt, S.L. Bennett, W.J. Huisman, M. Zwanenburg, D.-M. Smilgies, J.J. De Yoreo, W.J.P. van Enckevort, P. Bennema, and E. Vlieg, to be published.