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Report:

We have recently started a research program to obtain knowledge of the atomic/molecular scale structure of ionic crystals growing from solution. We have, so far, investigated two isomorphous systems; KDP (potassium- dihydrogen phosphate; KH_2PO_4) and ADP (ammonium- dihydrogen phosphate $NH_4H_2PO_4$). KDP family crystals are primarily used for laser applications, like optical switching and frequency conversion.

The Hartman-Perdok growth theory is very successful in predicting the growth morphology of crystals. As a starting point this theory uses the bulk crystallographic structure, assuming particular interactions between the constituents. This simple theory, however, cannot predict the exact atomic or molecular structure of surfaces. Relaxation and reconstruction of the surface are ignored and hence, their effect on the morphology. The availability of third-generation synchrotron radiation sources makes it possible to look accurately at the atomic structure of solid -liquid interfaces using surface X-ray diffraction.

The Hartman–Perdok theory predicts that pyramidal (101) and prismatic (100) faces of ADP are present during solution growth. The ADP (101) face can, in principle, terminate with an $[NH_4]^+$ (ammonium) or $[PO_4]^{3-}$ (phosphate) layer, or both. AFM (atomic force microscopy) measurements that we performed have shown that the height of the steps on the

(101) faces of ADP corresponds to the thickness of double layers, which means that only *one termination is present.*

The ADP (101) crystals were mounted in a growth chamber, in an environment of saturated aqueous ADP solution, and kept at a constant temperature by a thermostat. The incoming and outgoing X-ray beams penetrate through a thin Mylar foil which can be pushed close to the crystal surface, leaving a thin layer of saturated solution between the crystal and the foil. Data sets were collected for two different energies 9 keV and 19 keV. In order to find the best signal to background ratio, beside choosing the optimal wavelength, we performed two different kinds of measurements:

- Glancing incoming angle and large outgoing angle of the X-ray beam
- Large incoming angle and glancing outgoing angle of the X- ray beam

The second method yielded a 10 times better signal to background ratio.

The integrated intensities at various values of the diffraction index *l* along a CTR are determined by rotating the crystal about the surface normal and measuring the number of diffracted photons. To obtain structure factor amplitudes from the integrated intensities, different geometrical and resolution corrections are necessary. Figure 1.1 shows measured structure factor amplitudes along the (10) CTR for ADP (101). Our data show that the surface layer of ADP (101) is $[NH_4]^+$ *terminated* in the growth solution.

A good fit of the data is obtained when small out-of-plane relaxations of the top layer are allowed and when a simple model for surface roughness on an atomic scale is included. Ammonium is relaxed inwards by 0.3 Å (towards to bulk) and phosphate is relaxed 0.2 Å outwards. It is interesting, but not understood, to see that the relaxation of the top layer has the opposite sign compared to the case of KDP (101) [1]. A publication of these results is being prepared.

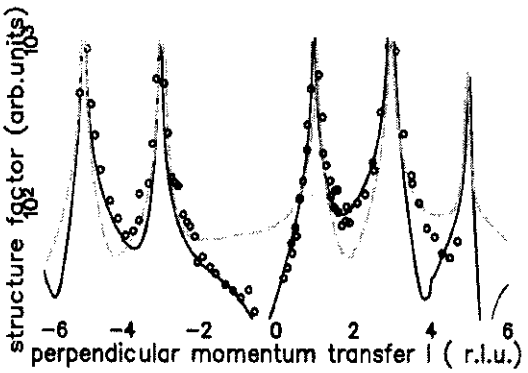

Figure 1.1: Structure factor amplitudes along (10)crystal truncation rod, for ADP (101). The solid line is the best fit starting from from a $[NH_4]^+$ terminated surface with relaxations included. Dashed line is calculation for a $H_2[PO_4]^-$ terminated one.

References:

[1] S. A. de Vries, P. Goedtkindt, S. L. Bennet, W. J. Huisman, M. J. Zwanenburg, D. M. Smilgies, J. J. De Yoreo, W. J. P. van Enckevort, P. Bennema and E.Vlieg, Phys. Rev. Lett. 80 (1998) 2229.