Names and affiliations of applicants (* indicates experimentalists):

S.A. de Vries*, P. Goedtkindt*, and E. Vlieg*
FOM-Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands
A. Stierle*
European Synchrotron Radiation Facility, Grenoble, France

Report:

      Crystal growth from solution is a very important process that is used from the laboratory to the industrial scale. Since the growth of crystals takes place at the crystal-solution interface, one expects the atomic structure at this boundary to play a primary role in the composition, growth and morphology of the crystal. Hardly any atomic-scale experimental data exist to verify this.

      In a previous experiment [I] we have performed an interface atomic structure determination of a potassium dihydrogen phosphate (KH_2PO_4, KDP) crystal in its aqueous growth solution [2]. We found that the $\{101\}$ faces are terminated by a layer of K^+ ions and not by $H_2PO_4^-$ groups, resolving a long-standing issue that could not be predicted by theory. This explains why trivalent metal ion impurities like Fe^{3+} and Cr^{3+} have little effect on the growth of this surface (they are repelled by the K^+ ions), while the growth on the (100) surface (that also contains PO_4^{3-} ions) is largely blocked. The presence of such impurities influences thus the macroscopic growth morphology of KDP.

      This time we have studied the interface' *in situ* during growth with and without impurities and for different supersaturations. 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 cylindrical part with wall thickness of 0.5 mm and a diameter of 1 cm (transmission geometry). We used an X-ray energy of 21 keV, which was chosen as an optimum in the signal to background ratio. For higher energies the background scattering from the bulk crystal rapidly goes up, while for lower energies the attenuation in the polycarbonate and solution becomes too strong. The saturation temperature (equilibrium) was 22°C. The crystals are grown by lowering the temperature of the system, which leads to supersaturation in the KDP solution (cooling 1°C leads to a supersaturation of -2 %). Heating leads analogously to dissolution of the crystal.

We first studied the growth of KDP(100). The microscopic origin of the growth blocking by $Fe^{3}+$ is not known. One possibility is that the Fe forms a (partly) ordered adlayer. To see whether this is true, we doped the solution with $Fe^{3'}$ ions and measured so-called crystal truncation rods (CTRs) of the crystal, similarly as was done in the structure determination of the clean system [1,2]. Unfortunately, we did not find significant changes on the CTR profile. From this we must conclude that if the $Fe^{3}+$ ions were adsorbed on the surface, they don't do this at lattice sites. It's also possible that only minute fractions of Fe adsorb at the growing interface (at step-edges for example) which would make the surface rough. To look at this we measured at appropriate positions along the diffraction rod, the peak height and width during growth with and without the presence of Fe in the solution.

In the second part of the experiment we looked at the growth of KDP(101). Impurities have a much smaller effect on this surface. Atomic-force microscopy experiments have shown that the growth mode of the (101) surface depends on the amount of supersaturation [3]. At supersaturations above 10 % terrace nucleation occurs. Again we have measured peak height and width during growth at different supersaturations. Unfortunately, during this part of the experiment there were a lot of beam losses due to RF cavity problems. This made it very difficult to follow the exact changes of our surface peaks after changing the temperature of the growth cell.

Since our set-up had changed in comparison with last year [l] to a transmission geometry, we were now able to measure the specular reflected beam. From this measurement it might be possible to determine whether there is any ordering of the solution against the growing crystal. Further analysis of the data is currently in progress.

[1] S.A. de Vries, P. Goedtkindt, E. Vlieg, and D.-M. Smilgies, ESRF Annual Report, Experiment SI-2 12, ESRF, Grenoble, France.
[2] S.A. de Vries, P. Goedtkindt, S.L. Bennett, 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., in press.
[3] J.J. De Yoreo, T.A. Land, and B. Dair, Phys. Rev. Lett. 73 (1994) 838.