pH-dependent liquid order at the solid-solution interface of KH$_2$PO$_4$ crystals

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We have determined the solid-liquid interface structure of the {101} and {100} faces of KH$_2$PO$_4$ (KDP) crystals in contact with a growth solution for three different pH values. Using surface x-ray diffraction data we find in all cases several liquid layers with varying degrees of lateral and perpendicular order. The structural changes are large for the {101} face and small for the {100}, which correlates with the changes in the macroscopic growth velocity of these faces. The changes at the {101} face are likely due to the pH-dependent competition between K$^+$ and H$_3$O$^+$ bonding. For the highest pH value crystalline preordering is observed.

The structure at a solid-liquid interface determines many important processes, such as crystal growth, wetting, lubrication, and catalysis.[1,2] Also from a fundamental point of view, the ordering of a liquid in contact with a solid is of interest.[3] In recent years several predictions from theoretical models and computer simulations have been verified using x-ray diffraction (XRD).[4,5] The ordering in the perpendicular direction ("layering") is found to be stronger than in the lateral direction, and extends typically over three to five monolayers.[6] The lateral ordering has only recently been determined for a few systems.[7,8]

Now that the global properties of solid-liquid interfaces have been confirmed, it is important to investigate the role of the solid-liquid interface in actual processes. Here we focus on crystal growth from solution, in which case the solvent is often found to determine the morphology of the crystal or the particular polymorphic form that is grown.[9] The crystal investigated here is potassium-dihydrogen-phosphate (KDP, KH$_2$PO$_4$),[10] whose morphology depends on the pH of the aqueous growth solution.[11] The growth morphology is determined by the {100} and {101} faces, where the growth velocity of the {101} face shows a quite strong dependence on the pH and is maximal for a stoichiometric solution (pH=4). The situation for the {100} face is less clear, which could be due to the high sensitivity of that face to impurities.[12]

For stoichiometric conditions the surface structure of the {100} and the {101} crystal face has been determined,[13] and for the {101} face in addition the interfacial liquid was found to show icelike ordering.[7] Here we report the solid-liquid interfacial structure of the {100} and {101} faces for three different pH values as determined using surface XRD. We find a remarkable large change for the {101} face, while the {100} face is hardly affected. We find evidence for ordering in the liquid, not only of the solvent but also of the solute molecules/ions. This is the first time that changes in the crystal growth morphology have been correlated with changes in the structure at a solid-liquid interface.

Surface XRD is very suitable for determining the atomic structure at the interface of a crystal surface with a solution, because of the large penetration depth of x rays.[2,5] The interface structure can be derived from structure factors measured along the so-called crystal truncation rods.[14] These rods originate from the interference sum between bulk and surface

signals of the crystal and include contributions from the ordered liquid at the interface. By including rods with different values for the in-plane momentum transfer, sensitivity to both the laterally ordered and disordered parts of the solid-liquid interface is achieved.[7] The experiments were performed at the DUBBLE beamline[15] at the European Synchrotron Radiation Facility (ESRF), Grenoble, using an X-ray energy of 16 keV. The setup consists of a growth chamber[16] coupled to a (2+3) diffractometer operating in a vertical geometry.[17] In order to increase the accessible range along a rod, data were collected with incoming angles 1° and 15°. A KDP crystal with a size of 3–6 mm was immersed in a saturated solution with specific pH; for each pH a new crystal was prepared. By adding H$_3$PO$_4$ or KOH, pH values of 3 or 6, respectively, were obtained.

To describe the surface unit cell of the {101} KDP crystal the following lattice vectors are introduced:[13]

$$\mathbf{a}_1 = \tfrac{1}{2}[111]_{\text{tetragonal}}, \quad \mathbf{a}_2 = \tfrac{1}{2}[\bar{1}1\bar{1}]_{\text{tetragonal}},$$

$$\mathbf{a}_3 = \tfrac{1}{2}[\bar{1}01]_{\text{tetragonal}}.$$

The corresponding reciprocal lattice vectors $\mathbf{b}_j$ are defined by $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. The momentum transfer vector is then denoted by $\mathbf{Q} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ with (hkl) the diffraction indices. The index l is the direction perpendicular to the surface, each rod is labeled by indices (hk).

We collected data sets for pH=3, pH=4.4, and pH=6 for both the {101} and the {100} face. Each data set of the {101} face consists of the (00), (10), (01) and (20) rods, with a total of 250 reflections. The P$_1$ symmetry of the {101} surface means that equivalent reflections are absent. However, the reproducibility for different incoming angles for the same reflection is 8%. The measured intensities were converted into structure factors by applying a standard procedure.[18] The parameters describing our models were fitted to experimental structure factors using a least-squares method employing the ROD surface crystallographic software.[19]

Figure 1 shows part of the data measured on the {101} face. There is a remarkably large difference between the three pH values, therefore the interface structure depends strongly on the pH of the solution. In contrast to this, the data acquired from the prismatic {100} face are the same for
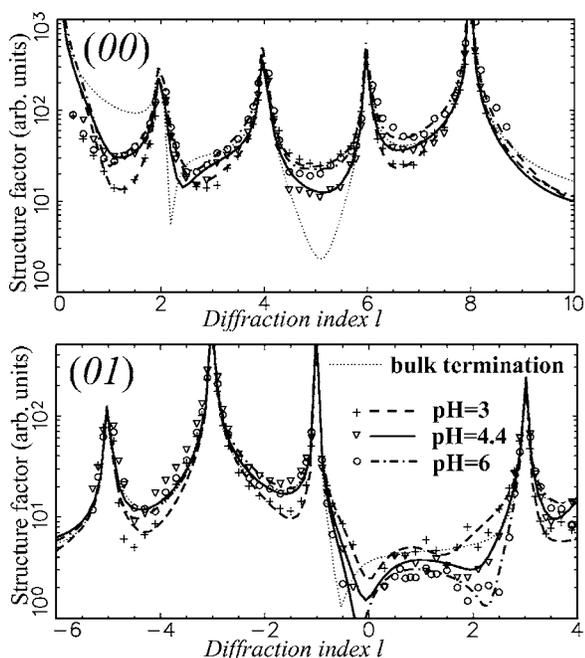
FIG. 1. Measured structure factors (symbols) along the (00) and (01) rods of the {101} face. The negative l values are obtained by inverting the structure factors according to Friedel's rule. The curves represent the best fit models for the measured data and for a bulk-terminated crystal.

all pH values within the estimated accuracy (not shown). We therefore conclude that for this face the structure is the same for the three pH values.

In order to determine the interface structures, we fitted the data using models that describe both sides of the solid-liquid interface,[7] as shown schematically in Fig. 2. For the crystalline part, the occupancy and position of the atoms near the interface is modeled. The different degrees of ordering of the interfacial liquid layers is modeled using (where necessary) anisotropic Debye-Waller parameters. Layers without in-plane ordering were modeled by giving these a very large ($\sim$1000) in-plane Debye-Waller parameter. The solution consists of water molecules and the various ions from KDP and the added components. Since x rays probe the electron density, the data are only moderately sensitive to the atom type. We can therefore initially model the liquid by using
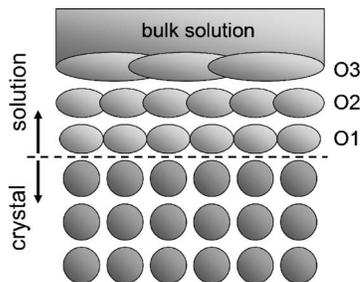

FIG. 2. The schematic structure at a solid liquid interface at which the liquid is evolving towards a bulk liquid over a few layers. The partial order in the layers closest to the crystal surface is modeled using anisotropic Debye-Waller parameters.

only layers of oxygen atoms (ignoring the hydrogen in the water for which the x rays are insensitive). If the occupancy of these oxygen atoms (labeled O1, O2, etc.) is found to be higher than 1, this is an indication that the corresponding layer contains heavier atoms. We found that surface roughness is negligible.

Since there is no significant variation in the data as a function of the pH value for the {100} face, we mention the fit results here only briefly; a more extensive discussion will be given elsewhere.[20] In agreement with earlier results,[13] we find that the crystal is bulk terminated with negligible relaxation. The more precise data obtained here further show that the formation of an H bond between crystal and solution is the most important structural feature. This bond will not be affected by the pH value, explaining the constant structure of the interface.

For the {101} face we start our discussion with pH=4.4, the stoichiometric value for which the full interface structure was determined earlier by Reedijk *et al.* using a water film with a thickness of only 22 Å.[7] We obtain essentially the same results, thus a thin film can be representative of a solid-liquid interface. The topmost K^+ and $H_2PO_4^-$ layers show small relaxations, and there are four water layers visible of which the first two are highly ordered ("icelike"). There are only differences in the lateral position of layers O1 and O2 and the occupancy of O1. In the present analysis we find two similar minima in the least-squares optimization, one of which is the same as that reported by Reedijk *et al.*, but another one yields an O2 position in which the distance to the K^+-ion is a more realistic 2.38 Å (compared to 1.97 Å). Table I shows the optimum parameters together with the earlier results, and Fig. 1 shows the best fit. The position of O1 is near the extrapolated lattice position of a next K^+ ion, suggesting that this layer partly consists of K^+ ions instead of water molecules. The occupancy, however, is only 0.63 assuming water at this location, so that the fraction of K is 0.3 at most.

For pH=6 we start the fit using the same model, but we find that in this case a high electron density in the first liquid layer is required in order to obtain a good fit. Now the position (in fractional coordinates) of O1 of (0.84, 0.15, 1.37) is even closer to the extrapolated position of a bulk K^+ ion of (0.875, 0.125, 1.375) and the occupancy for O1 is larger than 1. Replacing the O atom by a K^+ ion, we get essentially the same fit with a K occupancy of 0.56, making it likely that a substantial part of this site is occupied by K^+ ions. Other significant differences with pH=4.4 are a much lower order in layer O2 and a lower perpendicular order in O3. The fit results are shown in Fig. 1 and in Table I.

For pH=3 a low electron density in the first layer is required to obtain a good fit and the lateral position differs from that expected for K^+, thus ruling out a significant K^+ concentration at this location ($<$15%). The order in layers O2 and O3, by contrast, is increasing. This occurs at a height corresponding to the bulk-extrapolated position of $H_xPO_4^{-(3-x)}$. Together with the relatively high occupancy value in layer O2, this suggests that layers O2 and O3 contain a high concentration of $H_xPO_4^{-(3-x)}$. The lateral order in these layers is much less than in layer O1, as expected from

TABLE I. Best fit parameters for the {101} face. All positions (x, y, z) are expressed as fractions of the unit cell parameters, except Δz which is in Å with respect to an unrelaxed bulk position. Values with asterisks are fixed. The layers O1-O4 represent water layers, but two alternative fits are listed as well: in layers O2-O3 at pH=3 a fit assuming P layers and in layer O1 at pH=6 a fit with a K layer. In both cases, mainly the occupancy value is changed. The origin is chosen such that K has unrelaxed coordinates (0.75, 0.25, 1.25).

Layer	Par.	pH=3	pH=4.4	pH=6	Ref. 7
O4	z	1.63(8)	1.61(8)	1.67(6)	
	$B_{\parallel}$ [Å²]	1000*	1000*	1000*	1000*
	$B_{\perp}$ [Å²]	470(240)	505(100)	283(104)	
	Occ.	7(4)	5(4)	5(3)	
O3/P	x	0.51(2)	0.48(2)	0.43(2)	0.5
	y	0.32(5)	0.41(3)	0.05(3)	0.47
	z	1.50(1)	1.54(1)	1.52(2)	1.48
	$B_{\parallel}$ [Å²]	49(4)	35(4)	26(9)	12
	$B_{\perp}$ [Å²]	12(6)	18(5)	39(30)	160
	Occ.	1.0(2)/0.55(3)	1.0(2)	2(1)	0.7
O2/P	x	0.02(1)	0.00(1)	0.06(2)	0.2
	y	0.87(9)	0.86(4)	0.63(5)	0.77
	z	1.46(1)	1.46(1)	1.43(2)	1.44
	B [Å²]	22(8)	21(7)	197(20)	1.1
	Occ.	1.7(4)/0.9(3)	1.5(3)	1.0(2)	1.4
O1/K	x	0.88(2)	0.86(2)	0.84(3)	0.88
	y	0.32(9)	0.23(3)	0.15(2)	0.13
	z	1.36(1)	1.37(1)	1.37(1)	1.39
	B [Å²]	1.16*	1.16*	1.16*/1.4*	1.1
	Occ.	0.38(6)	0.63(6)	1.34(8)/0.56(3)	2.1
K	Δz [Å]	0.10(4)	0.06(9)	−0.04(4)	0.09
	z	1.260(4)	1.256(9)	1.246(4)	1.26
	B [Å²]	1.4*	1.4*	1.4*	1.4
	Occ.	0.74(3)	0.85(3)	0.71(3)	0.69
PO₄	Δz [Å]	0.00(2)	0.02(2)	0.04(2)	0.02
	z	1.125(2)	1.127(2)	1.129(2)	1.13
	Occ.	0.93(2)	0.96(2)	0.86(3)	0.93
	B_P [Å²]	0.85*	0.85*	0.85*	0.85*
	B_O [Å²]	1.16*	1.16*	1.16*	1.16*
	χ^2	2.66/2.67	2.68	2.69/2.50	

the larger distance to the surface. The picture that emerges is that $H_x PO_4^{-(3-x)}$ ions diffuse in this layer, residing relatively long at the locations given by O2 and O3. Note that the position of layer O3 of (0.51, 0.32, 1.50) is close to the bulk-extrapolated position of PO_4 of (0.5, 0.5, 1.5), but the disorder means that the positions in this and the O2 layer are not well defined. The orientation of the PO_4 ions should be random, meaning that from an x-ray point of view the oxygen atoms are effectively invisible.[21] In the fit model, we therefore replace the O by a P atom only. Table I lists the corresponding occupancy values, all other parameters are unchanged.

The changes in the interface structure as a function of pH are most easily seen in a z-axis projection of the electron density in which the liquid contribution depends on the in-plane order through the Debye-Waller parameter.[7] Figure 3 shows the results where the laterally ordered part of the liquid is represented by the dashed curves and where the solid curves show the perpendicular ordering. The small relaxations in the topmost K^+ and $H_2PO_4^-$ layers of the crystal are in full agreement with earlier results.[7,13] In the liquid part we observe a few ordered layers of which the first two show such a strong lateral order that these layers appear to be chemisorbed. The most striking effect is the density in the first "liquid" layer, for which at pH=6 both the density and the position point to a well-ordered K^+ layer. At pH=4.4 there may be some remains of this layer, but the density is much lower and the position agrees less with a (partial) K^+

a) pH=6

K$^+$

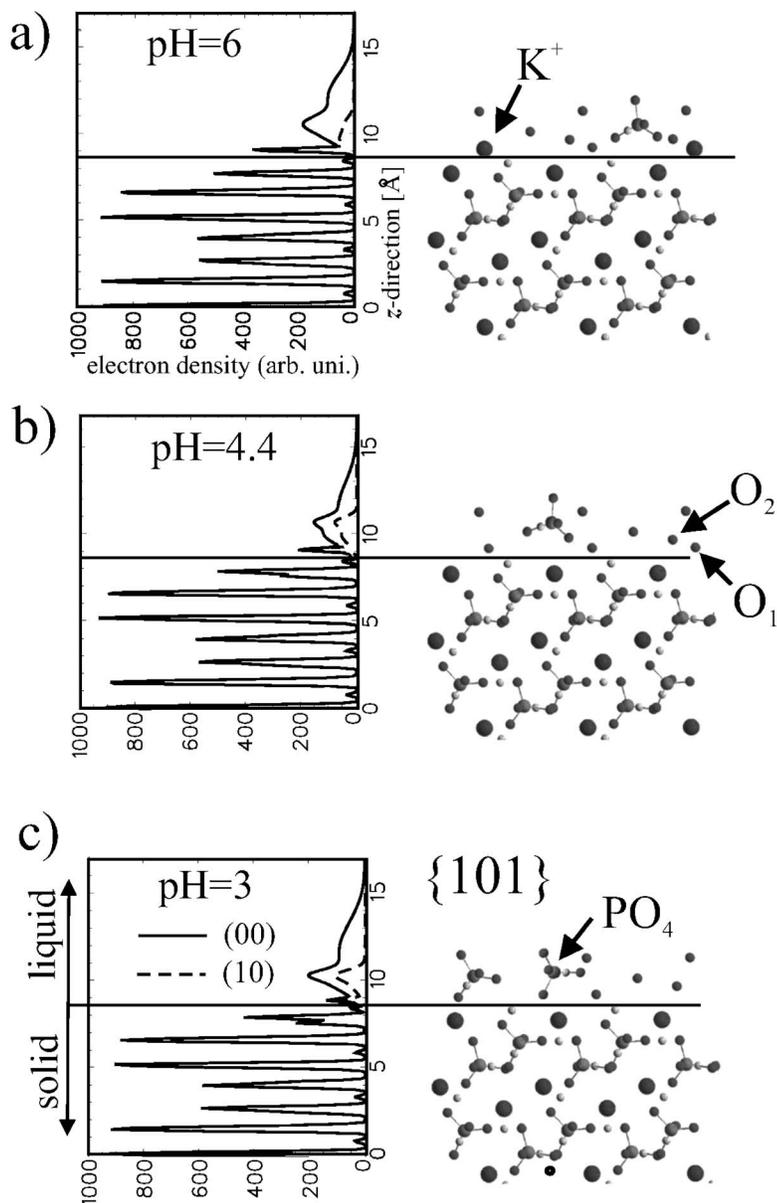electron density (arb. uni.)

z-direction [Å]

b) pH=4.4

O$_2$

O$_1$

FIG. 3. A schematic of the interface structure of the {101} face (right) together with the z-projected electron density distribution (left) for the three pH values. The solid curves denote the layers with perpendicular order, the dashed curves show the density of layers with lateral order corresponding to the (10) rod.

c) pH=3

liquid

solid

—— (00)

- - - - (10)

{101}

PO$_4$

layer, so it is likely that a significant fraction of this layer is occupied by O atoms (e.g., in the form of H_3O^+ ions). This agrees with the "icelike" layers reported at this pH.[7] At pH=3 this layer has largely disappeared.

How can we understand this behavior of the first liquid layer? One can start from two different points of view: electrochemical or crystallographic. The KDP{101} crystal terminates in a K^+ layer, thus from an electrochemical point of view the first liquid layer is expected to contain *negative* ions. This, however, has only limited validity because there is no net surface charge: the topmost K^+ layer is followed by two $H_2PO_4^-$ layers and another K^+ layer. The potential experienced by the solution is therefore much weaker than in the case of a genuinely charged layer and no normal electrochemical double layer is expected. The crystallographic point of view leads to a different conclusion. In the bulk of the crystal, the K^+ layer is followed by a second K^+ layer, and

one would thus expect such a positive layer to be formed in the solution as well. The clearest experimental result is for pH=6, and this strongly points to a K^+ layer in the solution. In this case the crystallographic point of view appears to be valid, and the data show in fact crystalline preordering in the solution. Such an arrangement with two positive layers is unexpected from the electrochemical point of view, but is of course possible due to the lateral crystallographic structure of the system. The extra, partial K^+ layer leads to a net charge, which should be compensated by negative ions ($H_2PO_4^-$) as indeed indicated by the high occupancy in layers 2 and 3.

The next question is, why does this K^+-layer only occur at pH=6? This pH value is obtained by adding KOH to the growth solution, but the moderate increase in K^+ concentration ($\sim$10%) seems too small to account for the large change in the K density in the first liquid layer. If we maintain the crystallographic point of view that this layer should

be positive, then the K^+ ions may be replaced by other positive ions. The best candidates for these are the H_3O^+ ions, the concentration of which increases by a factor 1000 going from pH=6 to pH=3. Their concentration remains much lower than that of the K^+ ions, but H_3O^+ has the advantage that it can form additional H bonds near the interface (e.g., to the topmost PO_4 groups in the crystal) and therefore be more favorable than K^+ in this position. We thus propose that the competition between the chemisorption of K^+ and H_3O^+ explains the observed pH dependence. To fully understand this behavior, one has to know the solution chemistry of this system[22] at the crystalline interface as a function of the pH value.

A second striking feature in the interface structure is the increasing lateral order in layer O2 (at a z position near 10 Å) for decreasing pH values. This layer (and O3) contains $H_xPO_4^{-(3-x)}$ ions, as derived from the position, the occupancy and from charge neutrality. If we assume that for decreasing pH the K^+ ions in the first liquid layer are indeed replaced by H_3O^+ ions, the increased lateral order can be due to the directional nature of the H bonds between H_3O^+ and $H_xPO_4^{(3-x)}$.

The structural differences are expected lead to changes in growth rate of the {101} face, because the incorporation of ions during growth involves several kinetic barriers[23] that will change with the interface structure. In addition, surface diffusion will be affected by the structural changes.[24] However, the present data do not directly reveal this relation between structure and growth velocity. In fact, the structural changes are found to vary monotonically, while the growth velocity is changing nonmonotonically and has a maximum for the middle pH value. Understanding this fully requires detailed modeling of the growth process based on the structural information derived here. Unfortunately, at present no such modeling software is available. The fact that on the {100} face the changes in the interface structure are minimal agrees with the minimal changes in growth velocity as a function of pH for that face.

In summary, we have shown that it is possible to observe the subtle structural changes that occur at the solid-liquid interface of a crystal as a function of the solution composition by using XRD and a high-quality crystal. The large changes at the {101} face and the absence of such changes at the {100} face as a function of pH correlate with the fact that the changes in the macroscopic growth velocity are large for the {101} and small for the {100} face. We find that chemisorption of solution ions occurs for both the {101} and {100} faces. These observations provide a good (but challenging!) starting point for a theoretical modeling of such interfaces in which the solution chemistry is taken into account.

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[1] B. Bhushan, J. N. Israelachvili, and U. Landman, Nature (London) **374**, 607 (1995); E. Johnson, Science **296**, 477 (2002).

[2] E. Vlieg, Surf. Sci. **500**, 458 (2002).

[3] F. Spaepen, Acta Metall. **23**, 729 (1975); D. W. Oxtoby, Nature (London) **347**, 725 (1990).

[4] E. Vlieg, in *Nanoscale Structure and Assembly at Solid-Fluid Interfaces*, Vol. 1, edited by X. Y. Liu and J. J. De Yoreo (Kluwer, Dordrecht, 2004), p. 31.

[5] P. Fenter and N. C. Sturchio, Prog. Surf. Sci. **77**, 171 (2004).

[6] M. F. Toney, J. N. Howard, J. Richer, G. L. Borges, J. G. Gordon, O. R. Mclroy, D. G. Wiesler, D. Yee, and L. B. Sorensen, Nature (London) **368**, 444 (1994); W. J. Huisman, J. F. Peters, M. J. Zwanenburg, S. A. de Vries, T. E. Derry, D. L. Abernathy, and J. F. van der Veen, *ibid.* **390**, 379 (1997); S. E. Donnelly, R. C. Birtcher, C. W. Allen, I. Morrison, K. Furuya, M. Song, K. Mitsuishi, and U. Dahmen, Science **296**, 507 (2002).

[7] M. F. Reedijk, J. Arsic, F. F. A. Hollander, S. A. de Vries, and E. Vlieg, Phys. Rev. Lett. **90**, 066103 (2003).

[8] L. Cheng, P. Fenter, K. L. Nagy, M. L. Schlegel, and N. C. Sturchio, Phys. Rev. Lett. **87**, 156103 (2001); J. Arsic, D. Kaminski, N. Radenovic, P. Poodt, W. S. Graswinckel, H. M. Cuppen, and E. Vlieg, J. Chem. Phys. **120**, 9720 (2004).

[9] M. Lahav and L. Leiserowitz, Chem. Eng. Sci. **56**, 2245 (2001).

[10] J. J. De Yoreo, A. K. Burnham, and P. K. Whitman, Int. Mater. Rev. **47**, 113 (2002).

[11] L. N. Rashkovich and G. T. Moldazhanova, J. Cryst. Growth **151**, 145 (1995); S. K. Sharma, S. Verma, B. B. Shrivastava, and V. K. Wadhawan, *ibid.* **244**, 342 (2002).

[12] T. A. Land, T. L. Martin, S. Potapenko, G. T. Palmore, and J. J. De Yoreo, Nature (London) **399**, 442 (1999).

[13] 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. **80**, 2229 (1998).

[14] I. K. Robinson, Phys. Rev. B **33**, 3830 (1986).

[15] M. Borsboom *et al.*, J. Synchrotron Radiat. **5**, 518 (1998).

[16] S. A. de Vries *et al.*, J. Cryst. Growth **205**, 202 (1999).

[17] E. Vlieg, J. Appl. Crystallogr. **31**, 198 (1998).

[18] E. Vlieg, J. Appl. Crystallogr. **30**, 532 (1997).

[19] E. Vlieg, J. Appl. Crystallogr. **33**, 401 (2000).

[20] D. Kaminksi, N. Radenovic, M. A. Deij, W. J. P. van Enckevort, and E. Vlieg, Cryst. Growth Des. (to be published 2006).

[21] A calculation shows that phosphate ions with random orientation give nearly the same intensity as a single phosphor atom.

[22] M. K. Cerreta and K. A. Berglund, J. Cryst. Growth **84**, 577 (1987).

[23] X. Y. Liu, E. S. Boek, W. J. Briels, and P. Bennema, Nature (London) **374**, 342 (1995).

[24] J. J. De Yoreo, T. A. Land, and B. Dair, Phys. Rev. Lett. **73**, 838 (1994).