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Compression versus expansion on ionic crystal surfaces

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We have determined the structure of the {101} face of ammonium dihydrogen phosphate (ADP) in aqueous solution by the use of surface x-ray diffraction. We find that a layer of ammonium ions terminates the {101} face of ADP, followed by a layer of phosphate ions. For a proper description of the experimental data, relaxation in these two layers needs to be included. The ammonium layer is relaxed inward by 0.34 ± 0.13 Å while the dihydrogen phosphate layer is relaxed 0.27 ± 0.11 Å outward. Comparing our results with earlier experiments on potassium dihydrogen phosphate KDP {101}, we find both similarities and differences between these two isomorphous crystals. The most striking difference is the reversal of the direction of relaxation of the outmost layer. Hydrogen bonding in ADP is a likely cause for this difference.

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The macroscopic shape of a crystal is largely determined by its structure on an atomic or molecular scale. Current theories that predict the growth shape of a crystal (in particular the Hartman-Perdok theory and its further developments) are therefore based on the bulk crystallographic structure.[1] These theories ignore the role of deviations from the bulk structure at the growth interface. This neglect arises largely from the lack of experimental knowledge about the atomic structure, in particular for the case of growth from solution. However, by using the present generation of synchrotron radiation sources, x-ray diffraction is now starting to provide quantitative information about surface relaxation, crystal termination, and the role of impurities for crystals growing from solution.[2]

In this paper, we report the surface structure of the {101} face of ADP (ammonium dihydrogen phosphate, $NH_4H_2PO_4$). This is a crystal of the KDP (potassium dihydrogen phosphate, KH_2PO_4) family, which is of interest because of its use in optical switching and frequency conversion in laser applications and its large role in fundamental studies of crystal growth from solution.[3]

Only very limited knowledge about the surface structure of such ionic crystals is available. By comparing our results with earlier experiments on KDP {101},[2] we can now look at the structural trends in this type of crystals. In both cases the {101} crystal face terminates with positive groups. The most striking difference is that the expansion of the top layer of KDP reverses to compression for the case of ADP.

The Hartman-Perdok theory correctly predicts[4,5] that the pyramidal {101} and prismatic {100} faces determine the growth morphology of ADP [Fig. 1(a)]. In this paper, we focus on the {101} face, which can, in principle, terminate by an $[NH_4]^+$ (ammonium) or a $[H_2PO_4]^-$ (dihydrogen phosphate) layer, or both [Fig. 1(b)]. In order to test the latter possibility, we have performed atomic force microscopy (AFM) measurements. These show molecularly flat terraces with steps of 5.3 Å in height (Fig. 2), which is equal to the interplanar distance d_{101}. If two terminations occur simultaneously, steps of 2.7 Å should exist and therefore we conclude that *only one termination is present*. Which termination cannot be determined from our AFM data, and therefore we performed *in situ* x-ray diffraction experiments at beamline ID32 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

Samples with as-grown surfaces were etched in ultrapure water for a few seconds and then regrown for 10 min in a slightly supersaturated aqueous solution. Because of the high solubility of ADP, the preparation of the samples required a number of etching-regrowth cycles in order to obtain the large and molecularly flat terraces necessary for the x-ray diffraction experiment. The ADP {101} crystals were mounted in a growth chamber[6] filled with saturated aqueous ADP solution, which was kept at a constant temperature of 22 °C using a water bath thermostat. The incoming and outgoing x-ray beams penetrated a thin Mylar foil, which was placed 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 x-ray energies: 9 and 19 keV. The signal-to-background ratio was quite low, since ADP contains mainly light elements, while the thin liquid layer produced significant background scattering. Finding the best signal-to-background ratio requires optimizing the x-ray energy and the incoming angle. In surface x-ray diffraction experiments, one typically uses small incoming angles. Here we also acquired data with large incident and small exit angles and found that the resulting sharper line profiles[7] had a 10 times better signal-to-background ratio.

In order to denote the ADP {101} surface and the x-ray reflections, we define a unit cell whose primitive lattice vectors $\{\mathbf{a}_i\}$ can be expressed in the terms of the conventional tetragonal lattice vectors ($a=7.50$ Å and $c=7.55$ Å) as

$$a_1=\frac{1}{2}[111]_{\text{tetragonal}},\quad a_2=\frac{1}{2}[\bar{1}1\bar{1}]_{\text{tetragonal}},$$

$$a_3=[\bar{1}01]_{\text{tetragonal}},$$

with

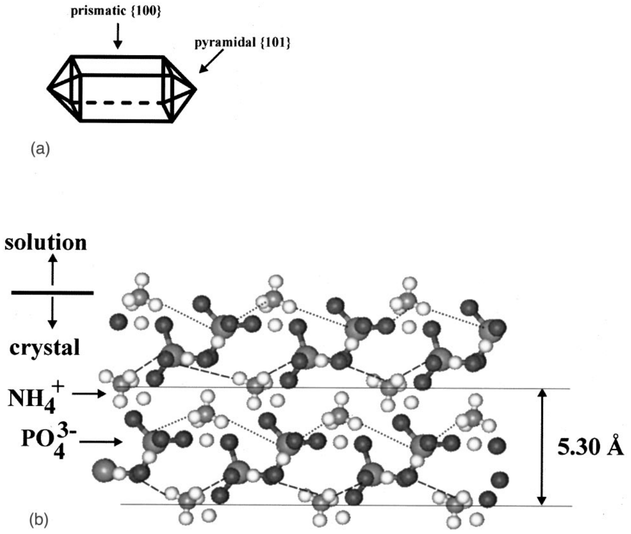

FIG. 1. (a) Growth morphology of an ADP crystal with the prismatic {100} and pyramidal {101} faces indicated. (b) Schematic side view of the pyramidal face {101}. The smaller tetragonal groups represent ammonium ions; the bigger tetragonal groups are phosphate groups. Dotted lines represent layers with ammonium termination, while dashed ones show layers with the phosphorous groups on top. The minimum step height on a surface with a single termination is 5.30 Å.

$$|a_1|=|a_2|=\sqrt{\tfrac{1}{2}a^2+\tfrac{1}{4}c^2},\quad |a_3|=\sqrt{a^2+c^2}.$$

The 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 expressed in reciprocal space as $\mathbf{Q}=h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3$ for the diffraction indices (*hkl*). With our unit cell definition the diffraction index pair (*hk*) refers to the in-plane component of $\mathbf{Q}$ and the index l to the out-of-plane component.

Integrated intensities of various reflections were determined by rotating the crystal about the surface normal and measuring the number of diffracted photons. For a flat crystal surface, there is a continuous intensity distribution along the l direction, the so-called crystal truncation rods (CTR's).[8]

The integrated intensities are converted into structure factor amplitudes by applying the necessary geometrical and resolution corrections.[7] The validity of this procedure is demonstrated by the fact that we were able to normalize data with small or large incoming angle on the same relative scale. The values for the negative l part of a rod are obtained using Friedel's rule.

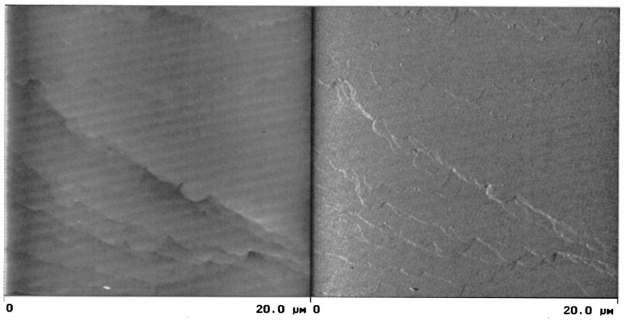

FIG. 2. An AFM image of the ADP {101} crystal surface after etching in ultraclean water. Terraces are molecularly flat and separated by steps with a height of 5.30 Å.

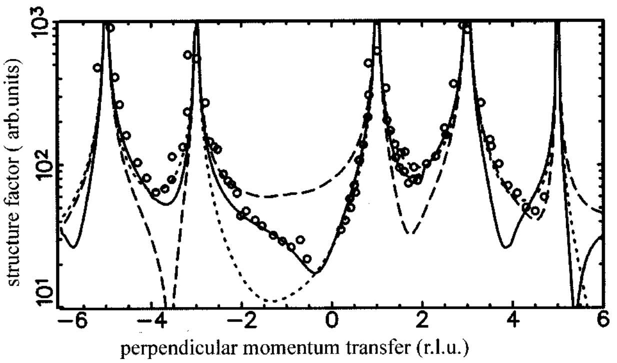

FIG. 3. Structure factor amplitudes along (10) rod for ADP {101} in solution, as a function of the perpendicular momentum transfer (diffraction index l), which is expressed in reciprocal lattice units. The dotted curve represents a calculation for a bulk $[NH_4]^+$-terminated surface and the dashed curve for a bulk $[H_2PO_4]^-$-terminated one [Fig. 1(b)]. The solid curve represents the best fit for the $[NH_4]^+$-terminated surface with relaxation of the two top layers included.

We measured in total 137 nonequivalent reflections, consisting of the (10), (01), (11) rod and in-plane data, with an agreement factor of 17% when averaged over all measurement conditions. Figure 3 shows the measured structure factor amplitudes of the (10) rod.

We first address the issue of the termination of the crystal surface. In Fig. 3 the structure factors calculated for the two possible bulk terminations of the {101} surface are compared with the data. The only fitting parameters in these cases were a scale factor and the surface roughness. The Debye-Waller factors were fixed at the bulk values. The fitting was done using the ROD program.[9] As Fig. 3 shows, neither $[NH_4]^+$ termination (dotted curve, $\chi^2=2.4$) nor the $[H_2PO_4]^-$ termination (dashed curve, $\chi^2=5.5$) yields a satisfactory fit, although the $[NH_4]^+$ appears to be the best. In order to obtain a good fit, it is essential to include relaxation of the two top layers of this surface. Including this, a good fit for the $[NH_4]^+$ termination (solid curve) was obtained with a $\chi^2=1.6$ for the entire data set. The relaxation values are listed in Table I. For the $[H_2PO_4]^-$ termination, we could not obtain a satisfactory fit ($\chi^2=5.1$). Including relaxation in more layers did not significantly improve our best fit. We also tried

TABLE I. Comparison of the top-layer relaxation of the two isomorphous {101} faces of ADP and KDP (Ref. 2). Minus and plus signs mean that the ionic layer is relaxed towards the bulk or towards the solution, respectively.

Growth layer	ADP Relaxation [Å]	KDP Relaxation [Å]
$[NH_4]^+/K^+$	-0.34 ± 0.13	$+0.10\pm0.05$
$[H_2PO_4]^-$	$+0.27\pm0.11$	$+0.04\pm0.05$

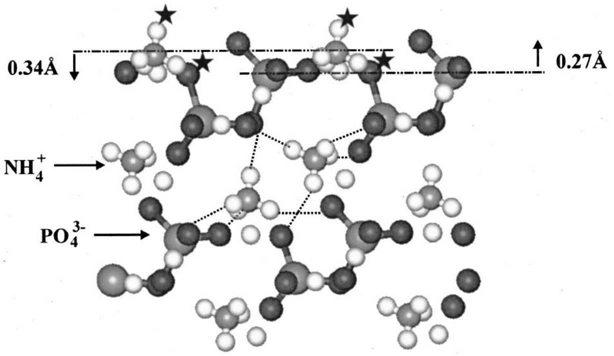

FIG. 4. Schematic side view of the {101} face showing the relaxation of the top layers. Bigger tetragonal groups represent phosphate groups, and smaller tetragonal groups represent ammonium groups. Dotted lines indicate hydrogen bonds between ammonium and phosphate groups in the bulk structure. Small stars indicate two groups with one hydrogen bond broken, due to the termination at the surface.

several other surface configurations,[5] including one with double ammonium layers on top, but none of them gave a satisfactory fit.

In our model we treated the phosphate as a fixed group, since our data are not accurate enough to treat the P and O atoms independently. The $[PO_4]^{3-}$ ions are expected to be very rigid as compared to the interionic movements. The ammonium ion is also treated as a group, because x-ray diffraction is very insensitive to the hydrogen atoms. The liquid in direct contact with the {101} face is expected to show partial ordering.[10] It should therefore have a small contribution to the diffraction rods. In our case of only nonspecular rods, this contribution is found to be negligible.

Our data show that in the growth solution the surface of ADP {101} is terminated by a layer of $[NH_4]^+$. This ammonium top layer is relaxed by 0.34 ± 0.13 Å towards the bulk, and the topmost phosphate layer is relaxed outward by 0.27 ± 0.11 Å; see Fig. 4. The surface has a roughness of less than 0.13 Å as measured over a lateral length scale of 200 Å, which is in agreement with the AFM images (Fig. 2). The bulk spacing between the $[NH_4]^+$ and $[H_2PO_4]^-$ layers is 1.33 Å. Due to the relaxation, this distance is reduced to 0.72 Å at the surface. This compression of 50% does not lead to unphysical bond distances, because of the crystallographic packing (Fig. 4).

The single termination we find from x-ray diffraction agrees with the AFM results (Fig. 2). The steps on the surface are always from one $[NH_4]^+$ layer to the next. Since the surface free energy is the main factor determining the crystal growth shape,[11] knowing which steps are realized is important.

Aguilo and Woensdregt used a point-charge model and nonrelaxed atom positions to predict the stability of various faces of ADP.[4] Even though they favored a growth mode in which two terminations occur simultaneously, they found the $NH_4{}^+$ termination to be the most stable, in agreement with our experimental results.

We can compare ADP {101} with the isomorphous KDP {101} surface.[2] For KDP {101} the crystal also terminates with a positive layer K^+. Even though these are the only two ionic crystals on which results of this type have been obtained, this termination in a positive layer appears to be a trend. Table I lists the relaxation measured for ADP and KDP. Here we find significant differences: while for ADP the top layer moves inward, for KDP it relaxes outwards. For both systems, the second layer relaxes outwards. The ADP surface relaxes more strongly than KDP. The two top layers thus have the same charge, but are otherwise completely different. The second layer consists in both cases of $[H_2PO_4]^-$, and this layer shows similar behavior.

The hydrogen bonding of the ammonium in ADP may cause the difference between KDP and ADP. This hydrogen bonding is absent in the case of KDP. In the bulk, the four hydrogen atoms of the ammonium group form hydrogen bonds to the oxygen ions of four neighboring phosphate groups (Fig. 4). At the ammonium-terminated surface, however, one of those hydrogen bonds is broken, leading to a broken bond in the top layer (ammonium) and a broken bond in the third layer (phosphate). Stars in Fig. 4 indicate these bonds. The large inward relaxation of the top layer reduces the bond distance between the associated nitrogen and oxygen atoms from 3.17 to 2.97 Å. This is very close to the value of 2.91 Å for the N-H-O hydrogen bond in bulk ADP. We thus propose that the driving force for the large inward relaxation of the surface ammonium groups is the formation of an extra hydrogen bond with the lower-lying phosphate groups, as a compensation for the bonds that are broken due to the crystal termination. In this case, the bonds of the ammonium group will no longer form a symmetric tetrahedron. We cannot determine this deformation experimentally, because the hydrogen atoms are largely invisible for the x rays. Presumably this effects wins from the tendency to form hydrogen bridges with the H_2O molecules above the surface.

It would be helpful if these ideas could be tested by model calculations. However, unlike the situation for crystals with other bonding types (metallic, covalent, molecular), there are no theoretical models that are sufficiently accurate to make general predictions on the behavior of surfaces of ionic crystals, neither in vacuum nor in an aqueous environment. We hope that our experimental results will stimulate the development of such theories, because ionic crystals are as important and common (e.g., rocksalts) as crystals of the other types. This would be a starting point for an atomic-scale understanding of the growth and dissolution of ionic crystals, the interaction with the aqueous environment, and the role that is played by impurities.[12,13]

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