

CRYSTAL MORPHOLOGY OF ADP ($\text{NH}_4\text{H}_2\text{PO}_4$): A QUALITATIVE APPROACH

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The Hartman–Perdok theory enables one to establish the order of morphological importance of the ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) crystal faces from its crystal structure. Periodic Bond Chains (PBC's) have been obtained using the $\text{N}-\text{H}_\text{N} \cdots \text{O}$ strong bonds between the ionic $[\text{NH}_4]^+$ and $[\text{H}_2\text{PO}_4]^-$ crystallization units. The PBC's are parallel to $\langle 100 \rangle$, $[001]$, $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ and $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$. The F faces which grow slowly according to a layer mechanism, are $\{011\}$ and $\{010\}$. The elementary growth layer of $\{011\}$ is not uniquely determined. Two layers bounded by either $[\text{H}_2\text{PO}_4]^-$ or $[\text{NH}_4]^+$ ions are possible. Hence the growth form of ADP is prismatic. S forms are $\{112\}$ and $\{110\}$. Although the $\{0kl\}$ are theoretically expected to be S faces, they nevertheless exhibit for $k < l$ K face characteristics. Only the $\{0kl\}$ with $k > l$, which are typical of the so-called tapering, are S faces.

1. Introduction

ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) is an important ferro-electric and electro-optic compound, showing at first sight a rather simple habit of the prism $\{010\}$ and the bipyramid $\{011\}$ (fig. 1a). Sometimes crystals of ADP show additional $\{0kl\}$, with $k > l$, which is known as tapering (fig. 1b). The conditions under which the tapering may occur are not fully understood [1]. It is therefore necessary to deduce the influence of the crystal structure on the crystal morphology and to determine the surface configuration of the interfaces at which the growth process takes place. The most appropriate method to study this relation is based on the Hartman–Perdok theory [2]. This theory has been successfully applied to a variety of compounds, such as silicates [3,4], halides [5], oxides [6] and oxalates [7], etc.

According to the Hartman–Perdok theory crystal faces can be classified as F, S or K faces, being

parallel to respectively more than one, only one, or none of the Periodic Bond Chains (PBC's). These PBC's are uninterrupted periodic chains formed by strong bonds. Once the relation between the crystal structure and morphology is known, the additional effects of other factors on the morphology, such as impurities, acidity, supersaturation, etc., can be studied in more detail.

Strong bonds

ADP is tetragonal, space group $\bar{I}4_2d$, and its crystal structure data are listed in table 1. Strong bonds in the sense of the Hartman–Perdok theory are bonds between nearest neighbours in the first coordination sphere, which are formed during the crystallization. As bond strengths are inversely proportional to the corresponding bond lengths, other bonds than next neighbour ones are not considered as strong bonds. Their influence on the growth characteristics expressed by the classifica-

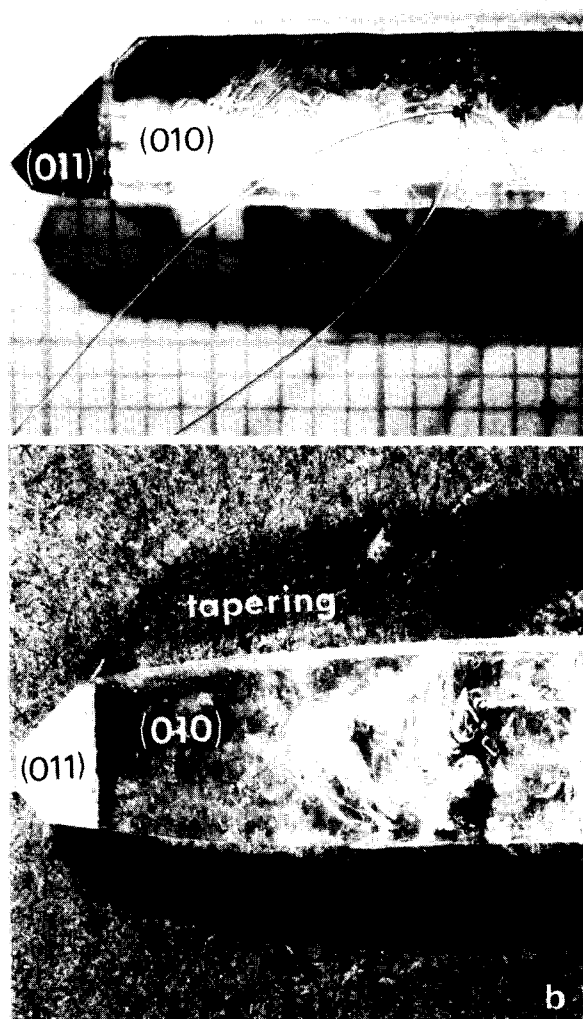


Fig. 1. Crystals of ADP ($\text{NH}_4\text{H}_2\text{PO}_4$). (a) Prismatic habit with prism {010} and bipyramid {011}. (b) Tapered crystals with additional {0kl}, with $k > l$.

tion into F, S or K faces can be neglected.

In supersaturated solutions of which the pH is about 4, the ADP is almost completely dissociated into $[\text{NH}_4]^+$ and $[\text{H}_2\text{PO}_4]^-$ ions [8]. Hence the only strong bond which merits consideration is the $\text{N}-\text{H}_\text{N} \cdots \text{O}$ bond between the crystallization units $[\text{NH}_4]^+$ and $[\text{H}_2\text{PO}_4]^-$. The other bonds between constituent atoms of the $[\text{H}_2\text{PO}_4]^-$ and $[\text{NH}_4]^+$ ions are not formed during crystallization. At lower or higher values of pH, the phosphate

Table 1

Crystal structure data of ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) according to Aijaz and Baur [18]

	Atomic coordinates		
	x	y	z
P	0.0	0.0	0.0
N	0.0	0.0	0.5
O	0.0843	0.1466	0.1151
H_N	0.998	0.089	0.563
H_O	0.25	0.150	0.125

Space group $\text{I}\bar{4}2\text{d}$, $Z = 4$; $a_0 = 0.74997$ nm, $c_0 = 0.75494$ nm.

Phosphor atoms $\text{P}(n)$ are numbered with $n = 1, \dots, 4$:
 $0, 0, 0; \frac{1}{2}, 0, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{3}{4}$.

Nitrogen atoms $\text{N}(o)$ are numbered with $o = 1, \dots, 4$:
 $0, 0, \frac{1}{2}; \frac{1}{2}, 0, \frac{3}{4}; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{4}$.

Hydrogen atoms $\text{H}_\text{O}(p)$ are numbered with $p = 1, \dots, 8$:
 $\frac{1}{4}, y, \frac{1}{8}, \frac{3}{4}, \bar{y}, \frac{1}{8}, \bar{y}, \frac{1}{4}, \frac{7}{8}; y, \frac{3}{4}, \frac{7}{8}, \frac{3}{4}, \frac{1}{2} + y, \frac{5}{8}, \frac{1}{4}, \frac{1}{2} - y, \frac{5}{8};$
 $\frac{1}{2} - y, \frac{3}{4}, \frac{3}{8}; \frac{1}{2} - y, \frac{1}{4}, \frac{3}{8}$.

Atoms in general positions such as $\text{O}(q)$ and $\text{H}_\text{N}(q)$ are numbered with $q = 1, \dots, 16$:

$x, y, z; \bar{x}, \bar{y}, z; \bar{y}, x, \bar{z}; y, \bar{x}, \bar{z}; \frac{1}{2} - x, y, \frac{1}{4} - z; \frac{1}{2} + x, \bar{y}, \frac{1}{4} - z;$
 $\frac{1}{2} + y, x, \frac{1}{4} + z; \frac{1}{2} - y, \bar{x}, \frac{1}{4} + z; x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2};$
 $\frac{1}{2} - x, \frac{1}{2} - y, z + \frac{1}{2}; \frac{1}{2} - y, x + \frac{1}{2}, \frac{1}{2} - z; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z;$
 $\bar{x}, y + \frac{1}{2}, \frac{3}{4} - z; x, \frac{1}{2} - y, \frac{3}{4} - z; y, x + \frac{1}{2}, \frac{3}{4} + z; \bar{y}, \frac{1}{2} - x,$
 $\frac{3}{4} + z$.

content may be to some extent present in the form of respectively H_3PO_4 or $[\text{HPO}_4]^{2-}$ and $[\text{PO}_4]^{3-}$. These species have to be considered as impurities, and may cause habit changes.

Each $[\text{H}_2\text{PO}_4]^-$ ion is bonded to six neighbouring ammonia ions by strong bonds. Two types of $\text{N}-\text{H}_\text{N} \cdots \text{O}$ bonds can be distinguished on the bases of different bond lengths: type f bonds with the relatively large $\text{N}-\text{H}_\text{N} \cdots \text{O}$ distance of 0.3170 nm, and type g with the shorter $\text{N}-\text{H}_\text{N} \cdots \text{O}$ distance of 0.2909 nm.

Each phosphate tetrahedral group is bonded to four others by the hydrogen atoms, H_O , forming the hydrogen bond $\text{O}-\text{H}_\text{O} \cdots \text{O}$, called type e (bond length 0.249 nm). This e type bond is not to be considered as strong bond, because the hydrogen type bond involved is too weak to overcome the ionic repulsion between the two negatively charged $[\text{H}_2\text{PO}_4]^-$ ions. Table 2 summarizes all the f, g and e type bonds, in which the tetrahedral groups of phosphates and ammonia are symbolized by respectively $\text{PO}(\dots)$ and $\text{NH}(\dots)$. Their

Table 2
Bonds of ADP (NH₄H₂PO₄)

Strong bonds		Type	Strong bonds		Type
PO(1)	NH(1)	f	PO(3)	NH(2)	g
	NH(1,00 $\bar{1}$)	f		NH(2,010)	g
	NH(2,00 $\bar{1}$)	g		NH(3)	f
	NH(2, $\bar{1}$ 0 $\bar{1}$)	g		NH(3,001)	f
	NH(4)	g		NH(4)	g
	NH(4,0 $\bar{1}$ 0)	g		NH(4,100)	g
PO(2)	NH(1)	g	PO(4)	NH(1)	g
	NH(1,100)	g		NH(1,010)	g
	NH(2)	f		NH(3,001)	g
	NH(2,00 $\bar{1}$)	f		NH(3, $\bar{1}$ 01)	g
	NH(3)	g		NH(4)	f
	NH(3,0 $\bar{1}$ 0)	g		NH(4,001)	f
Bonds		Type	Bonds		Type
PO(1)	PO(2)	e	PO(3)	PO(2)	e
	PO(2, $\bar{1}$ 00)	e		PO(2,010)	e
	PO(4,00 $\bar{1}$)	e		PO(4)	e
	PO(4,0 $\bar{1}$ $\bar{1}$)	e		PO(4,100)	e
PO(2)	PO(1)	e	PO(4)	PO(1,001)	e
	PO(1,100)	e		PO(1,011)	e
	PO(3)	e		PO(3)	e
	PO(3,0 $\bar{1}$ 0)	e		PO(3, $\bar{1}$ 00)	e
Bond lengths (nm)					
Type	Anion-anion		O-H _O ...O or N-H _N ...O		
e	0.4198		0.2496		
f	0.3775		0.3170		
g	0.4198		0.2909		

coordinates coincide with the coordinates of the central ions.

Pbc's

By transforming the tetragonal I cell of the ADP crystal structure into a P cell, as demonstrated for calcium oxalate by Strom and Heijnen [7], it is quite easy to determine all possible primitive PBC's, which are uninterrupted periodic chains of strong bonds not necessarily fulfilling the conditions of stoichiometry and nonpolarity [4]. Three types of primitive PBC's are possible resulting from different combinations of strong f and g bonds: (1) g-g, (2) g-f-g-f and (3) f-f.

Only four complete PBC's are present in ADP, parallel to $\langle 100 \rangle$, $[001]$, $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ and $\langle \frac{1}{2} \frac{1}{2} \frac{3}{2} \rangle$.

2. The PBC analysis

2.1. The $[100]$ PBC

Not only the two most prominent crystal forms of ADP, i.e. $\{010\}$ and $\{011\}$, but also the $\{0kl\}$ of the tapered crystals are parallel to the $[100]$ PBC. There are three different PBC configurations all parallel to the a -axis, having a period of 0.74997 nm. The main difference among the three derives from the type of bonding between the primitive $[100]$ PBC's.

2.1.1. Type A

In both primitive PBC's forming the complete $[100]_A$ PBC's the ammonia ions are situated half-way between two phosphate ions to which they are linked by g type strong bonds (see also fig. 2a). The two primitive PBC's are linked to each other by strong f type and weak e type bonds. For further details see also the schematic presentation in fig. 2a. In all the figures the type g bonds are indicated by solid lines, the type f bonds by dashed ones and the type e by dotted ones. An asterisk means that the indicated ion is situated on a slice boundary and shared by two slices.

2.1.2. Type B

The primitive $[100]_B$ PBC's are mutually linked by only f type strong bonds (fig. 2b). They have the same configuration as the primitive $[100]_A$ PBC's.

2.1.3. Type C

The $[100]_C$ PBC consists of two primitive PBC's having one ammonium ion situated in between two phosphate groups, just as in the case of the $[100]_A$ and the $[100]_B$ PBC's. The primitive PBC's are, however, mutually bonded by an e-type bond, instead of the f-type bond, as is the case in the $[100]_B$ PBC (compare fig. 2c with fig. 2b).

2.1.4. Slice configurations

Slice d_{020} . The slice thickness of the crystal

forms $\{010\}$ is halved to d_{020} due to the presence of the symmetry operators in the space group $I42d$. Within the slice d_{020} it is possible to define two $[100]$ PBC's, i.e. the $[100]_A$ and $[100]_B$ PBC. The surface configuration of the d_{020} slice does not depend on which of the two types is selected (see fig. 2d). The $\{010\}$ is an F face, as both types are linked by strong bonds parallel to $[001]$, e.g. $PO(1)-NH(4, 00\bar{1})$.

Slice d_{011} . It is always possible to trace any of the three different $[100]$ PBC types within the d_{011} slice boundaries, because each such PBC type is connected to its neighbours by strong bonds within those boundaries. There are two different d_{011} slice configurations, i.e. the d_{011}^A based on either the $[100]_A$ PBC or the $[100]_C$ PBC, and the d_{011}^B based on the $[100]_B$ PBC (see also fig. 2d). Therefore, regardless of one's choice for the $[100]$ PBC, $\{011\}$ is an F face. Energy calculations must show us which slice configuration is energetically the most stable (see also ref. [10]).

Slice d_{004} . For $\{001\}$ the slice thickness is reduced to d_{004} , within which it is impossible to connect a $[100]$ PBC to similar ones by strong bonds. Being parallel to two identical PBC's, i.e. $[100]$ and $[010]$, the face $\{001\}$ of ADP must have K-face characteristics [11].

Slice d_{0kl} . The $\{0kl\}$ forms with $k > l$ are genuine S faces, being parallel to either the $[100]_A$ PBC or the $[100]_B$ PBC. As can be seen in fig. 2d, neither type of $[100]$ PBC can be connected to its neighbours by strong bonds within the d_{031} slice boundaries. Even though the $\{0kl\}$ forms with $k < l$ are parallel only to the $[100]_C$ PBC, they are, nevertheless, K forms, because they are located on the $[100]$ zone between the K face $\{001\}$ and the F forms $\{011\}$ [11].

2.2. The $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ PBC

The halving of the period parallel to $\langle 111 \rangle$ is a result of the I cell symmetry of ADP. The $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ PBC has the shortest translation period of all PBC's, i.e. 0.65093 nm (see also table 3). The crystal forms $\{011\}$, $\{112\}$, $\{211\}$ and $\{110\}$ belong to the $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ zone. There is only one type of PBC parallel to $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ having the same structure as the primitive $\langle 100 \rangle$ PBC's (see fig. 3a).

Slice d_{011} . The d_{011} configuration defined by $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ PBC's is equivalent to that of the d_{011}^A configuration as described earlier in the section on the $[100]$ PBC (fig. 3b).

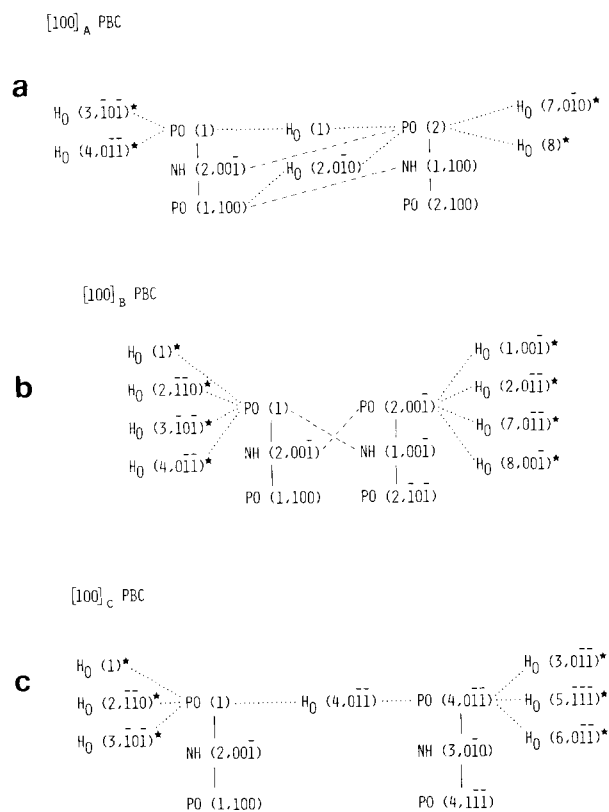
Slice d_{220} . The $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ PBC configuration does not fit within the slice boundaries of d_{220} (fig. 3b). Hence the $\{110\}$ is a K face in this zone.

Slice $d_{\bar{1}\bar{1}2}$. The $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ PBC can be defined within the slice of $d_{\bar{1}\bar{1}2}$. It is, however, not linked to any other $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ PBC (fig. 3b). The $\{112\}$ is to be considered as an S form.

Slice d_{211} . The $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ PBC is not present within the slice d_{211} , thus making $\{211\}$ a K form.

2.3. The $[001]$ PBC

The $[001]$ PBC can be considered as a combination of two complete PBC's marked α and β in fig. 4a, having shared one H_O ion. This is the only type PBC present parallel to $[001]$ and is built up of f-f bonds connected to each other by e-type



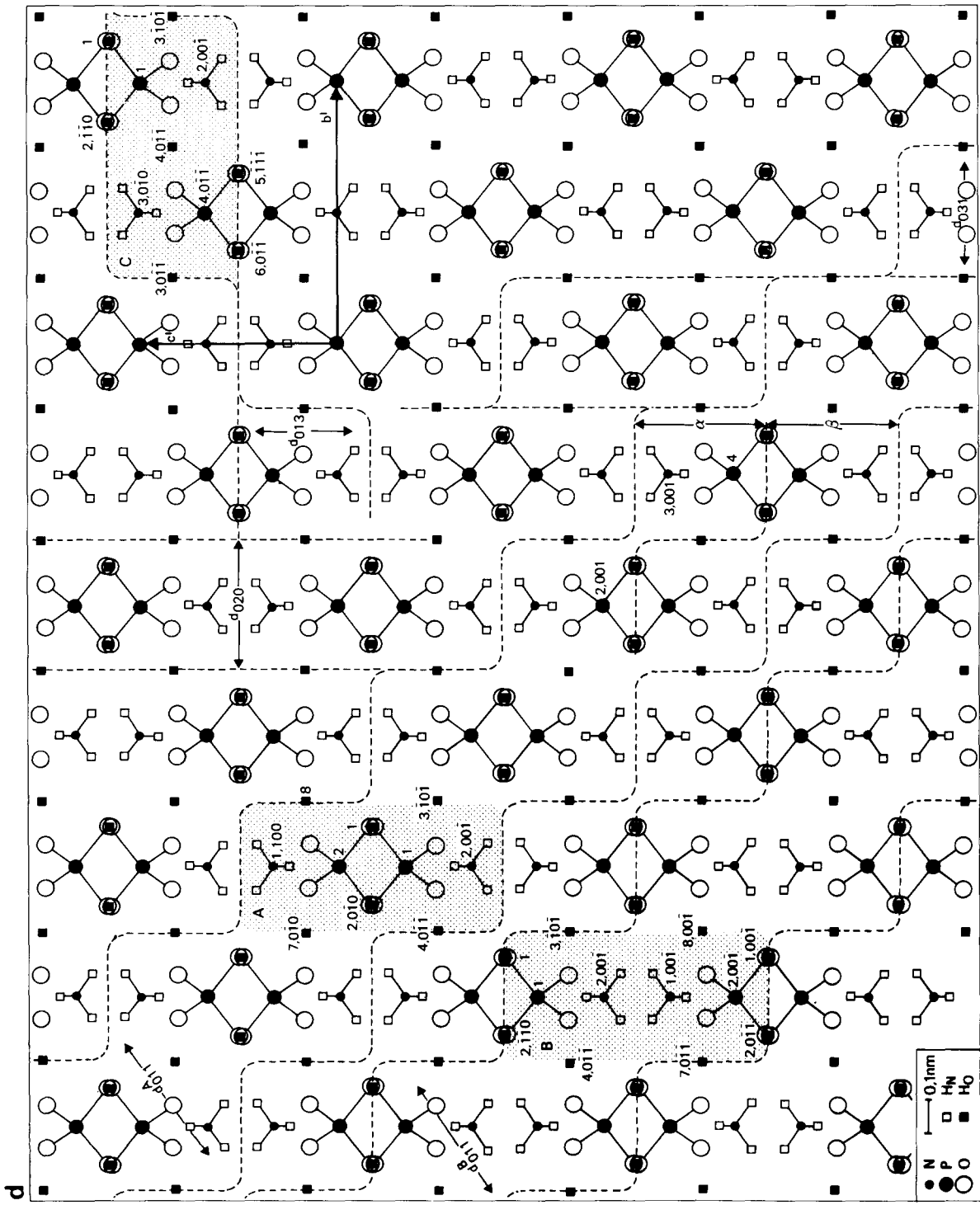


Fig. 2. (a) Schematic presentation of the [100]_A PBC. (b) Schematic presentation of the [100]_B PBC. (c) Schematic presentation of the [100]_C PBC. (d) [100] projection of the ADP crystal structure.

Table 3
PBC's and crystal forms of ADP

PBC	Period p (nm)	
$\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$	0.65093	
$\langle 100 \rangle$	0.74997	
[001]	0.75494	
$\langle \frac{1}{2} \frac{1}{2} \frac{3}{2} \rangle$	1.25043	
{ hkl }	Type	d_{hkl} (nm)
011	F	0.5321
010	F	0.3750
112	S	0.3075
121	K	0.3065
110	S	0.2652
013	K	0.2386
031	S	0.2373
001	K	0.1887
111	K	0.1085

bonds. It would not have been necessary to discuss this PBC in detail if it had no effect on the character of {110}, thus far classified as a K face in the $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ zone. But, as will be seen below, the [001] PBC does change the K status.

Slice d_{220} . Slices of d_{220} contain either [001] $_{\alpha}$ or [001] $_{\beta}$ PBC's. They determine the S character of {110} as none of these PBC types can be mutually linked by other non-collinear PBC's within the slice boundaries (fig. 4b).

Slice d_{020} . Within the d_{020} slice boundary the α and β [001] PBC's can be combined into one complete PBC as shown in fig. 4a. The presence of strong bonds parallel to $\langle 011 \rangle$ confirm the F character of {100} in this zone as well.

2.4. The $\langle \frac{1}{2} \frac{1}{2} \frac{3}{2} \rangle$ PBC

There is still another PBC which will not be discussed in detail as it does not provide us with any more information about the characteristics of the crystal faces already known. The PBC parallel to $\langle \frac{1}{2} \frac{1}{2} \frac{3}{2} \rangle$ has the hydrogen bond sequence f-g-f-g.

3. Discussion

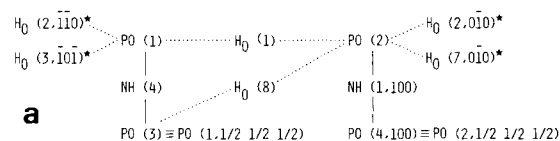
The morphological importance of crystal forms is often derived from the law of Donnay and

Harker. Morphological importance decreases according to decreasing corresponding interplanar spacing d_{hkl} as follows: {011}, {010}, {112}, {121}, {220}, {013}, {031}, {004}, {444}, etc. With the exception of the relative position of {031} this sequence more or less agrees with the observations on crystals grown in laboratory experiments.

Hartman [12] described the theoretical morphology of KDP (KH_2PO_4) which is isomorphous with ADP. The structure of KDP was compared to that of zircon (ZrSiO_4) without paying special attention to the presence of oxygen atoms. In this simplified structure, the following PBC's were found: [001], $\langle 100 \rangle$, $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ and $\langle 110 \rangle$, resulting in five F faces: {010}, {011}, {110}, {112} and {001}. Later Hartman found [13] that the [110] PBC had no physical meaning, as a result of which {112} and {001} became S faces. The present analysis clearly shows that the simplification led to erroneous results.

The absence of a symmetry centre has consequences for the surface configuration of certain slices. A crystal face such as (112) contains non-polar PBC's and has no dipole moment perpendicular to its surface. There is, however, a very distinct difference in the outermost surface structure between the top side, indicated by U for the slice d_{112} (fig. 3c) and the bottom, marked D. Such a slice with a surface structure which is not the same for both sides will be called enantiofacial, because it is always paired with another face, which has the reverse surface configuration. The faces (112) and $(\bar{1}\bar{1}\bar{2})$ form an enantiofacial pair. These faces have the same slice energy as their contents are identical. The diffusion length of adsorbed particles over the crystal surface will be different for the two sides. Hence their growth rates are equal, if they depend only on the attachment energy. Should the surface diffusion be the rate determining factor the

[1/2 1/2 1/2] PBC



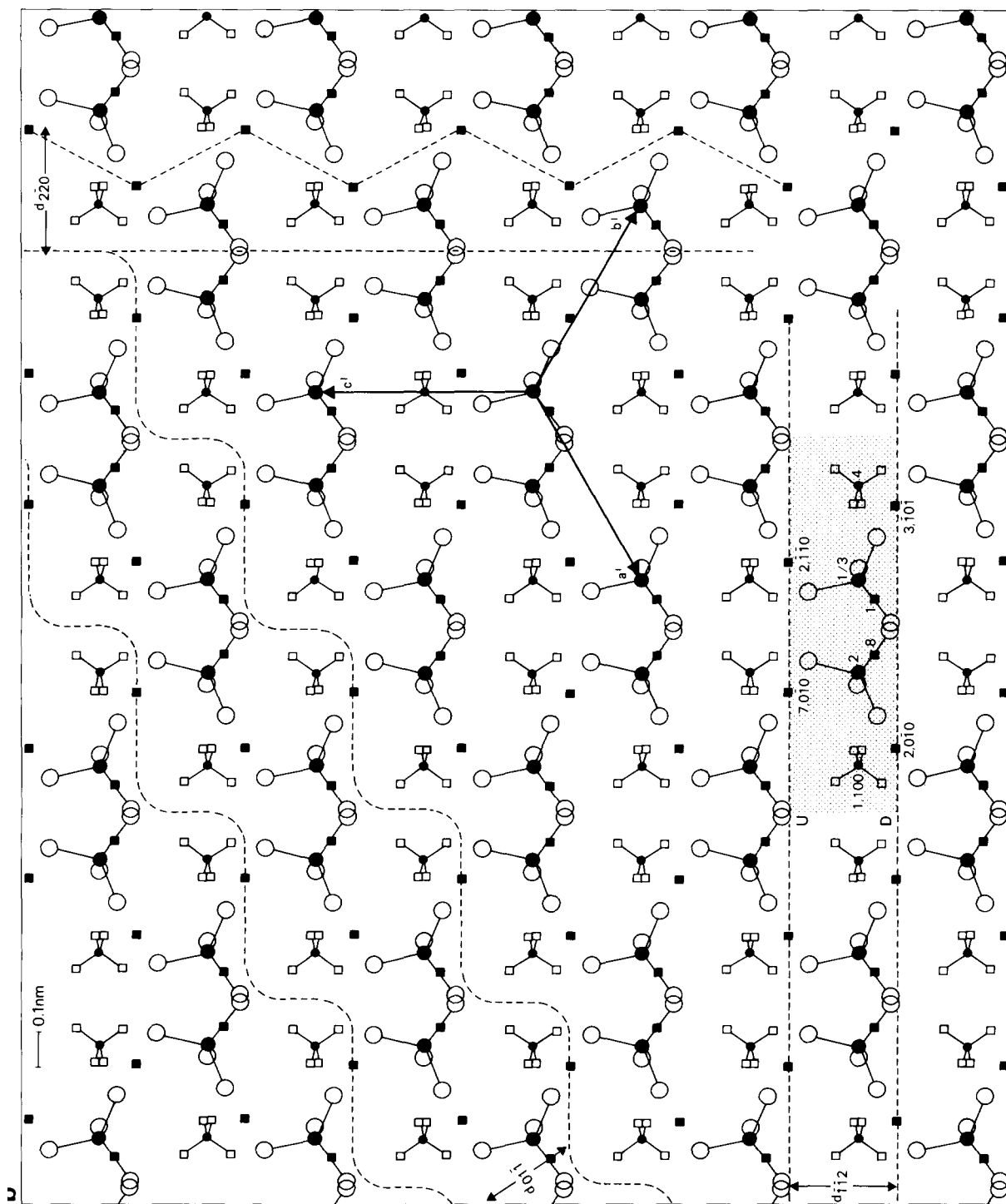


Fig. 3. (a) Schematic presentation of the $[111]$ PBC. (b) $[222]$ projection of the ADP crystal structure.

[001] PBC

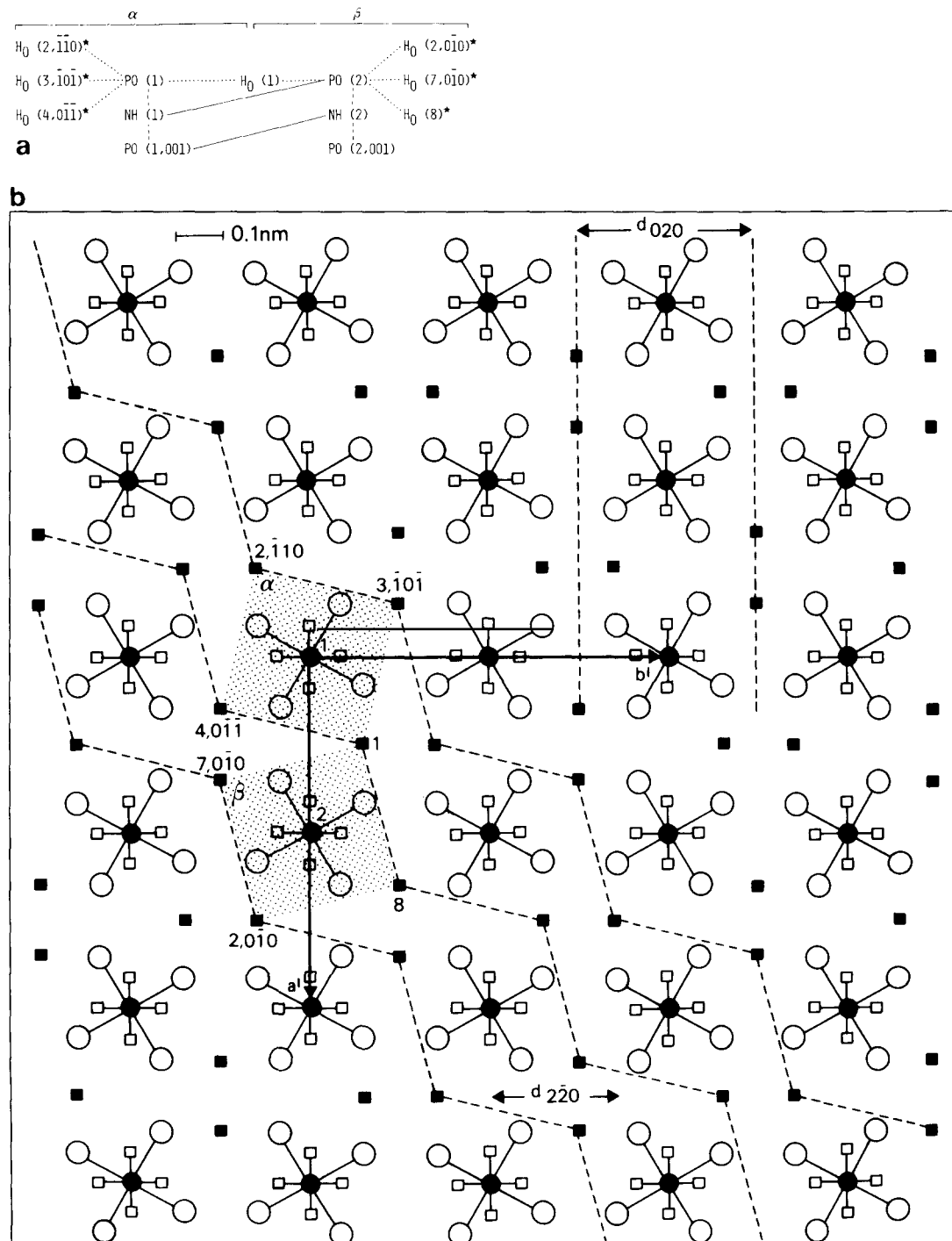


Fig. 4. (a) Schematic presentation of the [001] PBC. (b) [001] projection of the ADP crystal structure. The P atoms coincide with the N ones in this projection!

growth rates would be different. This has also been demonstrated by Cadoret and Monier [14], who applied the BCF theory to enantiofacial faces of compounds with the sphalerite or wurtzite structure.

Generally speaking only the $\{hkl\}$, with $h = 0 \vee k = 0 \vee l = 0$, in the ADP space group $I\bar{4}2d$, are not enantiofacial.

Bennema [15] demonstrated that spheres of ADP placed in supersaturated solutions at 40°C display parts of banded regions, which consist of small well defined separated flat areas, and are parallel to $[\bar{1}\bar{1}1]$ between (110) and (011) , $[\bar{1}\bar{1}\bar{1}]$ between $(\bar{1}10)$ and $(0\bar{1}\bar{1})$, $[1\bar{1}\bar{1}]$ between $(\bar{1}\bar{1}0)$ and $(0\bar{1}\bar{1})$, and $[\bar{1}11]$ between $(\bar{1}\bar{1}0)$ and $(0\bar{1}\bar{1})$. This limited number of zones does not correspond to the point group symmetry of ADP, from which the presence of eight differently oriented banded regions could be expected. The explanations by Dam et al. [16] that such bands are situated between F faces is incorrect since $\{110\}$, which was indicated as the starting or end point of the bands, is not an F but an S face. Neither is the assumption that there exist PBC's parallel to $\langle \frac{3}{2} \frac{1}{2} \frac{1}{2} \rangle$ in order to explain a secondary set of bands justified, even if hydrogen bonds are taken into account.

The presence of large $\{112\}$ faces on the spheres observed by Bennema [15] must be due to external factors, such as impurities and surface reconstruction. Being S faces they do not have the characteristics of a slowly growing crystal face.

Hartman and Heijnen [17] postulated a new growth mechanism for faces for which it is possible to define more than one surface structure. The F form $\{011\}$ of ADP is an example of such a face, of which the elementary growth layer is either bounded by positive $[\text{NH}_4]^+$ or negative $[\text{H}_2\text{PO}_4]^-$ ions. The layer with thickness $\frac{1}{2}d_{011}$, which is the difference between these two surfaces, has the characteristics of an F face, as there exist strong g-g hydrogen bonds, e.g. $\text{PO}(4)\text{-NH}(3, 001)\text{-PO}(2, 001)$, between the $[100]$ PBC's such as $\text{PO}(4)\text{-NH}(3, 001)\text{-PO}(4, 100)$. In fact the slice d_{011} can be divided in two F slices, α and β (see also fig. 2d). If their attachment energies do not differ too much, the growth of $\{011\}$ proceeds via slices of thickness d_{022} at increased rate. Once the attachment energies are known [10], one may dis-

cuss this effect in more detail.

The present study shows that the $\{011\}$ and $\{010\}$, which are the most prominent crystal forms on crystals grown in laboratory experiments, are F faces. They grow slowly according to a two-dimensional layer mechanism. The surface structure of the slice d_{020} is occupied positive $[\text{NH}_4]^+$ and negative $[\text{H}_2\text{PO}_4]^-$ ions. As discussed earlier the d_{011} slices are bounded by either positive or negative ions. The S forms are $\{0kl\}$, with $k > l$, $\{110\}$ and $\{112\}$. All other faces are K faces. An example of such a K face is (001) being parallel to two equivalent $\langle 010 \rangle$ PBC's.

The presence of the K face (001) situated between two F faces $\{011\}$ induces the K character to all faces $\{0kl\}$ with $k < l$. These faces are never present, in contrast with the S faces $\{0kl\}$ with $k > l$ which are typical for tapered crystals.

Although the hydrogen e-type bonds should in principle be neglected (see the section on strong bonds), for the sake of completeness we nevertheless reformulated the PBC construction taking also these bonds into account. The result of this, in our opinion erroneous supposition, was the appearance of one additional PBC parallel to $\langle 011 \rangle$,

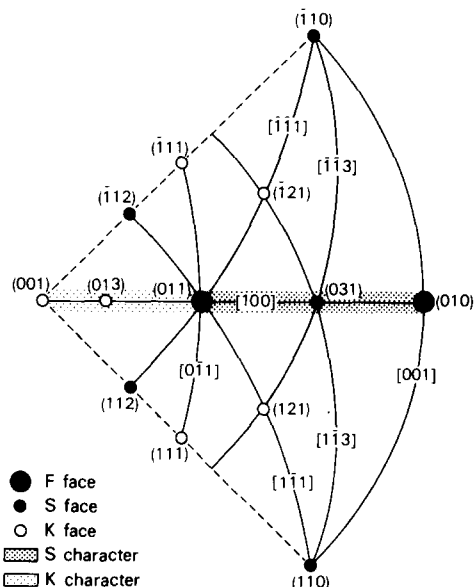


Fig. 5. Stereographic projection of ADP.

causing $\{211\}$ to become an S face instead of a K one.

The stereographic projection summarizes all the PBC's present, and the classification of the most prominent crystal forms (fig. 5).

4. Conclusions

(1) PBC's are present in the ADP structure parallel to the following directions: $\langle 100 \rangle$, $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$, $\langle 001 \rangle$ and $\langle \frac{1}{2} \frac{1}{2} \frac{3}{2} \rangle$.

(2) The crystal forms $\{011\}$ and $\{010\}$ normally present as the most important forms are F forms. Their presence can be derived from the influence of the crystal structure on the morphology.

(3) The $\{0kl\}$, with $k > l$, are all S forms. Their presence on tapered crystals must be due to external factors, such as the presence of impurities and conditions of supersaturation.

(4) The outer surface structure of $\{011\}$ consists of either $[H_2PO_4]^-$ ions or $[NH_4]^+$ ions. On the surface of $\{010\}$ both positive and negative ions are present.

(5) Other S forms are $\{112\}$ and $\{110\}$. All other forms, including $\{0kl\}$, with $k < l$, are K faces.

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