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Correlation between growth of high-index faces, relative growth rates and crystallographic structure of crystal

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Abstract. According to contemporary crystal growth theories, crystals are bound by low-index faces which are the most slowly growing. However, high-index faces are observed in crystal habits more and more often. In this paper the growth of high-index faces is analysed from a crystallographic perspective. It is shown that the crystallographic structure of a given crystal, expressed by the trigonometric function of appropriate interfacial angles, influences to great degree the crystallisation process and the morphology of crystals, in particular the behaviour of high-index faces. Additionally, it is concluded that at particular crystallographic structure of a crystal, a given high-index face may exist in the habit and develop its size, although it grows much faster than the neighbouring faces.

PACS. 81.10.Aj Theory and models of crystal growth; physics of crystal growth, crystal morphology and orientation

1 Introduction

Theoretically, a bulk crystal may possess an infinite number of faces. However, practically grown crystals possess a limited number of faces which are the slowest growing faces. In the past, many attempts have been made to correlate the morphological development of crystals with their internal structure. First, Bravais and Friedel, after many observations, established the Bravais-Friedel law [1,2]. This law reveals the correlation between the importance of a crystal face and its interplanar distance. According to this law the observed crystal faces are those with the largest interplanar distances. The larger the interplanar distance, the more important the corresponding crystal face. Later, it was shown, first by Niggli [3], then by Donnay and Harker [4] that this law is sometimes violated. Therefore, Donnay and Harker extended this law by considering the screw axis and the glide planes. The Bravais-Friedel-Donnay-Harker (BFDH) law often gives satisfactory description of the morphology of crystals. However, the drawback of the BFDH law is its purely geometrical character. Further, Hartman and Perdok [5] developed a more general theory based on an energetic hypothesis. The Hartman-Perdok (HP) theory introduces the concept of periodic bond chains (PBCs) which plays a key role in this theory. A PBC is an uninterrupted chain of bonds representing strong interactions between growth units in the crystal lattice. Three types of faces are distinguished by the classical HP theory: flat faces (F faces) – parallel to at least two non-parallel intersecting PBCs; stepped faces (S faces) – parallel to only one PBC; kinked faces (K faces) – not parallel to any PBC. According to this theory only the F faces are important for the crystal morphology. Later, Burton *et al.* described the transition of flat crystal faces to roughened faces at equilibrium as a function of temperature [6]. Further, the Hartman-Perdok theory was integrated with the theory of surface roughening [7,8] and the concept of connected net was introduced [9–11]. A connected net is a set of growth units connected by bonds constituting a network. Equivalent connected nets are separated by the interplanar distance d_{hkl}, corrected for the space group symmetry (according to the BFDH law). In other words this is the distance that separates physically identical surfaces. Connected nets can be derived from a so-called crystal graph, which is defined as an infinite set of points corresponding to the centres of the growth units with strong bonds between these points. Connected nets have edge free energies larger than zero in all crystallographic directions parallel to the net. Faces parallel to a connected net grow as flat faces (called F faces in the HP theory) below a specific roughening temperature and as rough rounded off faces above this temperature. In most cases the low-index faces of crystals are growing below their roughening temperature as flat faces with well-defined (*hkl*) orientation by a layer mechanism, like spiral growth or two-dimensional nucleation. High-index faces are not parallel to a connected net and have a roughening temperature equal to 0 K and, therefore, they grow as rough rounded off faces. In the other words high-index faces are fast-growing and therefore, they exist in the habit very rarely. The faces limiting the crystals are slow-growing faces *i.e.* low-index faces. However, high-index faces are observed

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in crystals. For example, the authors of the paper [12] describe the concanavalin A crystal with high-index face which appearance in the habit is very common. There are only few papers (*e.g.* [13]) in which an attempt to explain such a phenomenon is undertaken.

The aim of this paper is to show that the behaviour of both low-index and high-index faces is influenced, on one hand, by the growth environment which determines the relative growth rates, but on the other hand, by the geometry of the crystal as well. We present an analytical expression which explains the increasing in size of high-index faces and disappearance of low-index faces. All our considerations are in connection with the crystallographic structure of crystals.

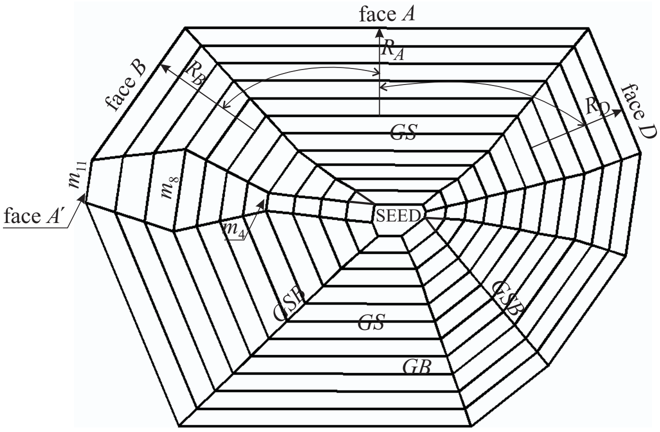


Fig. 1. Exemplary cross-section of a hypothetical 3D crystal with the considered face A and its neighbouring faces B and D; R_{A}, R_{B}, R_{D} – the normal growth rates of the faces A, B and D, respectively; α, γ – the interfacial angles; GB – growth bands; GS – growth sectors; GSB – growth sector boundaries; m_4 to m_{11} denote the consecutive growth bands on the face A′ growth sector.

2 Method of analysis

For crystals for which surface patterns cannot be observed by interferometry or AFM in or *ex situ*, for example, in a case of natural crystals or crystals grown from high-temperature solution, the internal morphology is very informative to investigate the growth processes. All changes or fluctuations of growth conditions occurring during the growth process are "recorded" in the crystal in a form of growth bands, growth sectors, growth sector boundaries, *i.e.* in a form of internal morphology which is revealed in crystal cross-sections. The internal morphology makes it possible to investigate the evolution of faces depending on relative growth rates as the growth bands appear in unknown time intervals. Straight boundaries between adjacent sectors correspond to constant relative growth rates of the faces whose sectors created this boundary. Bent boundaries between growth sectors indicate that the relative growth rates are not constant.

From the above it ensues that internal morphology revealed in crystal cross-section gives the possibility to analyse and follow the evolution of individual faces. For that reason, in order to investigate the behaviour of a given face, in particular a high-index face, we introduce the idea of the critical growth rate $R_{\mathrm{A}}^{\mathrm{crit}}$. The critical growth rate $R_{\mathrm{A}}^{\mathrm{crit}}$ is defined as the normal growth rate of the face A at which this face (shown in Fig. 1) preserves its size [14,15]. The critical growth rate $R_{\mathrm{A}}^{\mathrm{crit}}$ is expressed by the formula [14,15] which combines the growth rates of individual faces with the crystallographic structure of crystal represented by appropriate interfacial angles:

$$R_{\mathrm{A}}^{\mathrm{crit}} = \frac{R_{\mathrm{B}} \sin\gamma + R_{\mathrm{D}} \sin\alpha}{\sin(\alpha+\gamma)} \cdot \qquad (1)$$

The growth rates R_{B} and R_{D} are the normal growth rates of the faces B and D, respectively. The faces B and D are the neighbouring faces of the face A (Fig. 1). The angles α and γ are the angles between normals to the pairs of the faces: A/B and A/D (Fig. 1), respectively. As it was mentioned above, the critical growth rate $R_{\mathrm{A}}^{\mathrm{crit}}$ means the growth rate of the face A, situated between the faces B and D, at which this face preserves its initial size ($R_{\mathrm{A}}/R_{\mathrm{A}}^{\mathrm{crit}} = 1$). This may be observed on the example of the face A′ visible in Figure 1. Here, the ratio $R_{\mathrm{A'}}/R_{\mathrm{A'}}^{\mathrm{crit}}$, beginning from the seed up to the m_4 growth band, is equal to unity and, therefore, this face preserves its initial size. If the face A grows with the normal growth rate R_{A} smaller than $R_{\mathrm{A}}^{\mathrm{crit}}(R_{\mathrm{A}}/R_{\mathrm{A}}^{\mathrm{crit}} < 1)$, then the initial size of the face A increases. In the case of the exemplary face A′ (Fig. 1) the ratio $R_{\mathrm{A'}}/R_{\mathrm{A'}}^{\mathrm{crit}}$ changes its value becoming smaller than unity beginning from m_4 to m_8 growth band. It leads to the increasing in size of the face A′. When the growth rate R_{A} is greater than $R_{\mathrm{A}}^{\mathrm{crit}}(R_{\mathrm{A}}/R_{\mathrm{A}}^{\mathrm{crit}} > 1)$ the initial size of the face A decreases. In the case of the face A′ shown in Figure 1, the ratio $R_{\mathrm{A'}}/R_{\mathrm{A'}}^{\mathrm{crit}}$ is greater than unity, beginning from m_8 growth band till the end of the growth process. This is why this face decreases its size at this stage of growth.

Substituting the values of growth rates and angles appropriate for any face into equation (1) it is possible to evaluate the critical growth rates $R_{\mathrm{A}}^{\mathrm{crit}}$ for different faces of a given crystal. Having the critical growth rates $R_{\mathrm{A}}^{\mathrm{crit}}$ which correspond to changes in sizes of different faces, we draw them in one graph in a Cartesian system obtaining the so-called graph of the critical relative growth rates [16]. In the general case, the critical growth rates $R_{\mathrm{A}}^{\mathrm{crit}}$ are planes (or lines) which cross in the space of this graph. These crossing planes divide the graph into different regions. Each region corresponds to different appropriate relative growth rates and therefore, different changes in the habit. This means that, on the basis of such a graph, it is possible to analyse the behaviour of faces during the growth process depending on relative growth rates of appropriate faces. Moreover, it is possible to draw, using computer simulations, the external habits which correspond to each region of the graph, and the cross-sections of these habits (internal morphology). Such cross-sections are a very good complement to the graph of the critical relative growth rates, which allow us to follow changes of the growth sectors, growth boundaries and, finally, the whole habit, occurring in response to the changes of the relative growth rates of the individual faces.

In this paper, the described above method is applied to a concanavalin A crystal which is chosen as an example to investigate the behaviour of high-index faces which often appear in this crystal.

3 Results and discussion

In order to investigate the behaviour of high-index faces, let us consider, as an example, a lecithin protein concanavalin A crystal. This crystal belongs to the orthorhombic space group I222 with unit cell constants: a = 89.2 Å, b = 87.2 Å, c = 63.1 Å [17]. According to Moré and Saenger [18] the concanavalin A crystal is bound by low-index faces, in particular {100} and {010} faces. However, in reference [12], the authors suggest that the high-index faces $\{n1n\}$, where the value n ranged from 7 to 11, appear instead of the low-index {100} and {010} faces. Moreover, the authors found the $\{n1n\}$ faces of concanavalin A crystal to be macroscopically flat, in spite of high Miller indices. For this reason, this crystal is very interesting to investigate the presence and behaviour of high-index faces and was therefore chosen as a modelling crystal.

3.1 Different morphology evolution of concanavalin A crystal depending on relative growth rates

For the purpose of this article let us assume that in the concanavalin A crystal, besides low-index faces such as {100}, there exist high-index faces $\{n1n\}$, we assume that $n = 7$ (Fig. 2a). As the internal morphology is much more helpful in studying the changes of the crystal habit let us cleave the crystal shown in Figure 2a along the s line. In this way we obtain the cross-section of concanavalin A crystal shown in Figure 2b. It should be pointed out that the final crystal habit of this crystal with low-index faces and high-index faces shown in Figure 2 is considered as a model to study the existence of high-index faces. We note that all faces which appear in this habit were experimentally observed and reported [12,18].

As it is seen in Figure 2b, the high-index faces {717} have two neighbouring faces {100} and {001}. In order to investigate the behaviour of these faces and its dependence on relative growth rates and crystallographic structure of the crystal let us analyse the following critical relative growth rates: $R^{\text{crit}}_{\{717\}}/R_{\{100\}}$, $R^{\text{crit}}_{\{001\}}/R_{\{100\}}$ and $R^{\text{crit}}_{\{100\}}/R_{\{717\}}$. These critical relative growth rates allow us to analyse the changes in size of all faces appearing in this cross-section, *i.e.* {717}, {001} and {100}, respectively. However, in order to have all these dependences in one graph, aiming to have the same variables in all equations, we write the critical relative growth rates in the following forms:

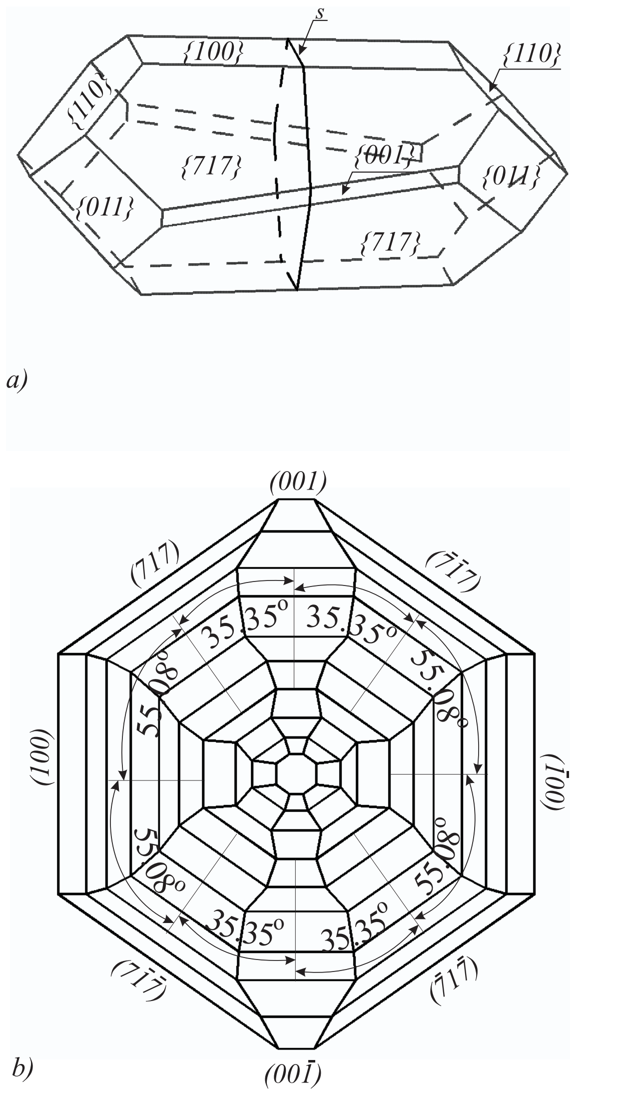


Fig. 2. (a) The theoretically assumed growth morphology of concanavalin A crystal with the considered high-index {717} face. The s line indicates the position of the cross-section presented in b); (b) The cross-section of concanavalin A. The values of the interfacial angles between normals to appropriate faces which appear in this cross-section are presented.

$$\frac{R^{\text{crit}}_{\{717\}}}{R_{\{100\}}} = 0.58 + 0.82\frac{R_{\{001\}}}{R_{\{100\}}}, \tag{2}$$

$$\frac{R_{\{717\}}}{R_{\{100\}}} = \frac{1}{1.23}\frac{R^{\text{crit}}_{\{001\}}}{R_{\{100\}}}, \tag{3}$$

$$\frac{R_{\{717\}}}{R^{\text{crit}}_{\{100\}}} = \frac{1}{1.75}\,. \tag{4}$$

The detailed explanation how these equations were derived is given in Appendix A.

Now, it is possible to draw these three critical relative growth rates in one graph – it is shown in Figure 3. The line 1 in this figure illustrates the dependence given by

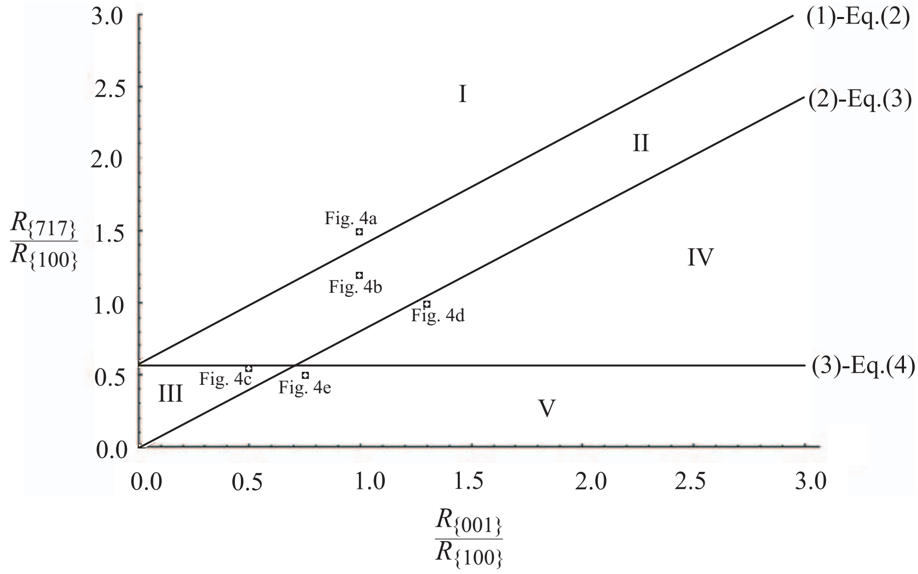


Fig. 3. The lines 1, 2 and 3 representing the critical relative growth rates: $R^{\mathrm{crit}}_{\{717\}}/R_{\{100\}}$, $R^{\mathrm{crit}}_{\{001\}}/R_{\{100\}}$ and $R_{\{717\}}/R^{\mathrm{crit}}_{\{100\}}$ given by equations (2, 3) and equation (4), respectively. The regions I, II, III, IV and V created by these crossing lines are regions of the appropriate relative growth rates corresponding to the growth of crystals of different morphologies, of which the cross-sections are shown in Figure 4. The relative growth rates for each of these cross-sections are marked and, additionally, they are presented in Table 1.

equation (2) (critical relative growth rate $R^{\mathrm{crit}}_{\{717\}}/R_{\{100\}}$), the line 2 – given by equation (3) ($R^{\mathrm{crit}}_{\{001\}}/R_{\{100\}}$) and the line 3 – given by equation (4) ($R_{\{717\}}/R^{\mathrm{crit}}_{\{100\}}$). These three crossing lines divide the space of the graph into five regions: I, II, III, IV and V as denoted in Figure 3. Each region corresponds to different changes in crystal habit, therefore, the analysis of these regions allows us to research the behaviour of all faces existing in the given cross-section shown in Figure 2b, in particular the behaviour of high-index face {717}. In order to make such an analysis easier, in Figure 4 we present the cross-sections of concanavalin A crystals, which correspond to each region of the graph. These cross-sections are obtained by computer simulation using program SHAPE (ver. 4.1.1. professional [19], the basic concepts of the software were published in Ref. [20]). We assume in our discussion that the growth process proceeds from identical seeds which possess all the faces appearing in final habits and moreover, that the individual faces are of the same size. As it is mentioned earlier, we focus in this paper on the changes in size of all faces which appear in the cross-sections, *i.e.* {717}, {001} and {100}. These sets may take different values of the growth rates, however, they are constant for each crystal for which the cross- section is presented in Figure 4 (it is assumed that the growth rate of a given face is constant during the growth of a single growth layer. Then, the distance between growth layers is proportional to the growth rate of the appropriate face). Consistently, the cross-sections presented in Figure 4 differ from each other by the relative growth rates $R_{\{717\}}/R_{\{100\}}$, $R_{\{001\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$, therefore, as the seeds grow, the crystals of different habits appear. The theoretically assumed values of these relative growth rates for each cross-section are presented in Table 1 and additionally, these values are marked in Figure 3.

First, we consider the region I. This region lies above all three lines of appropriate critical relative growth rates. This means that for the relative growth rates from this region, the sizes of faces {717} decrease while the sizes of the sets {100} and {001} increase. This is shown in Figure 4a. Here, the face {717} is the fastest growing face (the relative growth rate $R_{\{717\}}/R_{\{100\}} = R_{\{717\}}/R_{\{001\}} = 1.50$) and the face {717}, in compliance with our expectations, decreases its size – Figure 4a.

The region II (Fig. 3b) lies between three lines of the critical relative growth rates, namely above the lines 2, 3 and below the line 1. From this it follows, that for the relative growth rates from this region, the sets {717}, {100} and {001} increase their sizes. Such a situation is shown in Figure 4b. Here, the face {717} is also the fastest growing face ($R_{\{717\}}/R_{\{100\}} = R_{\{717\}}/R_{\{001\}} = 1.20$ – Tab. 1), as in the case of region I, however, in this case, the face {717} increases its size – Figure 4b. This unusual behaviour of this face may be explained based on crystallographic structure of this crystal represented by the interfacial angles α and γ. This is analysed in detail in Section 3.2. Here, we conclude that such a phenomenon occurs for particular relative growth rates only.

The region III (Fig. 3) is above the line 2 and simultaneously below the lines 1 and 3. Therefore, the growth with the growth rates from this region guarantees the increase in the sizes of the sets {717} and {001} and, simultaneously, the decrease of the size of the set {100}. Such a situation is shown in Figure 4c. Here we can see that the

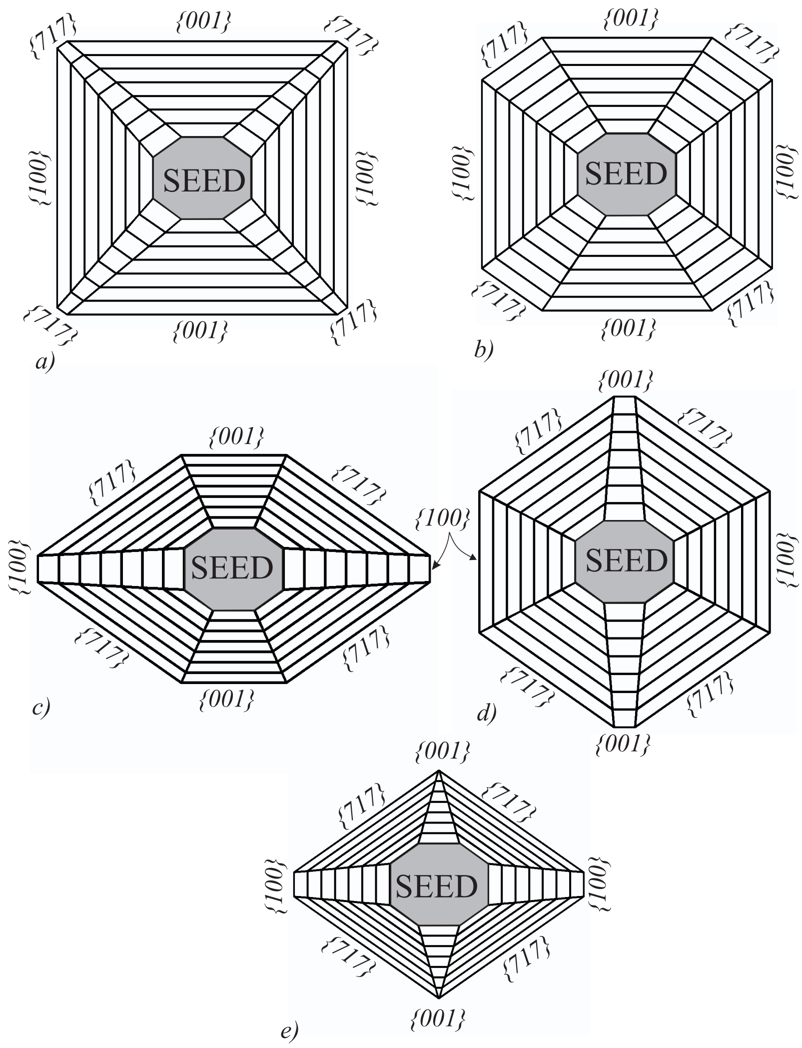


Fig. 4. The exemplary cross-sections of concanavalin A crystal habits corresponding to different regions of the graph of critical relative growth rates presented in Figure 3. For all these cross-sections the growth process begins from identical seeds. The number of growth bands and the time distance between them are the same. The appropriate relative growth rates for each cross-section are presented in Table 1 and, additionally, are marked in Figure 3.

Table 1. The theoretically assumed relative growth rates $R_{\{001\}}/R_{\{100\}}$, $R_{\{717\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$ for which appropriate cross-sections shown in Figure 4 are obtained and the changes in sizes of the individual sets of faces corresponding to appropriate regions of the graph presented in Figure 3. Symbol ↑ means that a given set increases its size in a given region of the graph; ↓ means that a given set decreases its size in a given region of the graph.

The relative growth rate: / Cross-section shown in:	$\frac{R_{\{001\}}}{R_{\{100\}}}$	$\frac{R_{\{717\}}}{R_{\{100\}}}$	$\frac{R_{\{717\}}}{R_{\{001\}}}$	Set of faces: {717}	{100}	{001}
Fig. 4a - region I	1.00	1.50	1.50	↓	↑	↑
Fig. 4b - region II	1.00	1.20	1.20	↑	↑	↑
Fig. 4c - region III	0.50	0.53	1.07	↑	↓	↑
Fig. 4d - region IV	1.30	1.00	0.77	↑	↑	↓
Fig. 4e - region V	0.76	0.50	0.66	↑	↓	↓

{717} face also increases in size, although it grows faster than one of the neighbouring set of faces, namely the set {001} (Tab. 1).

The region IV corresponds to increasing in size of {717} and {100} faces and simultaneously decreasing of the {001} face size. Such a situation is shown in Figure 4d. Here, the {717} face grows equally fast as one of the neighbouring set {100} (Tab. 1) and, in spite of this, the {717} face increases its size. For appropriate relative growth rates lying in the region V the {717} face increases its size and, at the same time, the faces {100} and {001} decrease their sizes as illustrated in Figure 4e.

In this section we have shown that for given relative growth rates $R_{\{717\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$ an unusual phenomenon occurs, namely the high-index face {717} of concanavalin A crystal develops its size although it grows faster than the neighbouring faces (Figs. 4b and c). In the next Section (3.2) we will analyse the connections of this phenomenon with the crystallographic structure of crystal.

3.2 Increasing in size of fast growing high-index face {717} in connection with the crystallographic structure of concanavalin A crystal

In the general case the analysis of the relations between the crystallographic structure of a crystal with the growth of high-index faces is based on the equation (1) transformed to the form:

$$\frac{R_\mathrm{A}}{R_\mathrm{A}^\mathrm{crit}} = \frac{\sin(\alpha+\gamma)}{\dfrac{\sin\gamma}{R_\mathrm{A}/R_\mathrm{B}} + \dfrac{\sin\alpha}{R_\mathrm{A}/R_\mathrm{D}}}\,. \tag{5}$$

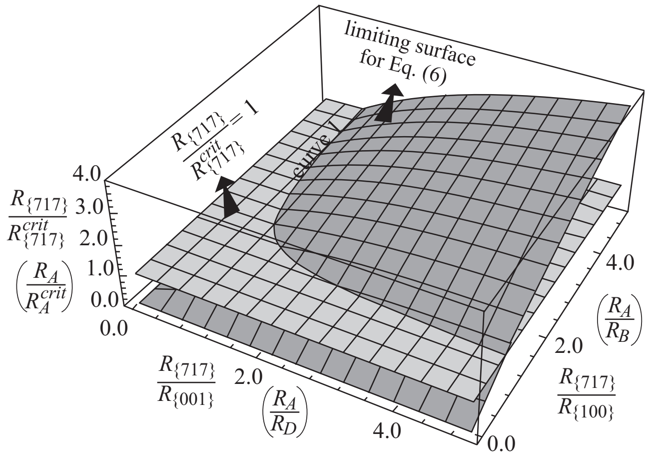
The physical meaning of equation (5) is that for $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit} < 1$, the face A increases in size; for $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit} = 1$, the face A preserves its size; for $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit} > 1$, the face A decreases its size (*cf.* the explanation concerning Eq. (1) – Sect. 2).

If we assume that the face A is a fast-growing high-index face, we are interested in whether the ratio $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit}$ may be smaller than unity at a given crystallographic structure of crystal for $R_\mathrm{A}/R_\mathrm{B} > 1$ and $R_\mathrm{A}/R_\mathrm{D} > 1$. In other words if the inequality given by:

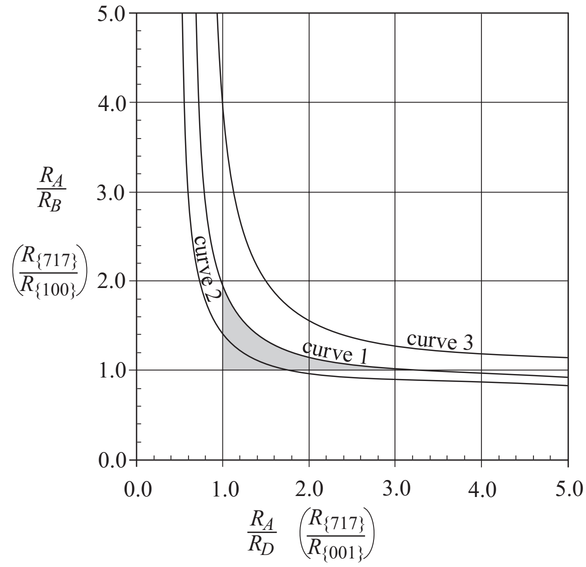
$$\frac{\sin(\alpha+\gamma)}{\dfrac{\sin\gamma}{R_\mathrm{A}/R_\mathrm{B}} + \dfrac{\sin\alpha}{R_\mathrm{A}/R_\mathrm{D}}} < 1 \tag{6}$$

is satisfied for given values of relative growth rates $R_\mathrm{A}/R_\mathrm{B} > 1$ and $R_\mathrm{A}/R_\mathrm{D} > 1$, then the given high-index face A increases in size growing faster than both neighbouring faces B and D for given crystallographic structure of crystal *i.e.* for appropriate angles α and γ.

The dependence given by equation (6) applied to a concanavalin A crystal, precisely to the considered high-index {717} face of this crystal, is presented in Figure 5a. If we substitute into this equation $\alpha = 35.35°$ and $\gamma = 55.08°$ (*cf.* Fig. 2), we obtain the dependence of $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit} = R_{\{717\}}/R_{\{717\}}^\mathrm{crit}$ on $R_\mathrm{A}/R_\mathrm{B} = R_{\{717\}}/R_{\{100\}}$



a)



b)

Fig. 5. (a) Dependence of the $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit}$ ratio on the relative growth rates $R_\mathrm{A}/R_\mathrm{B}$ and $R_\mathrm{A}/R_\mathrm{D}$ (Eq. (6)) applied for concanavalin A crystal ($R_{\{717\}}/R_{\{717\}}^\mathrm{crit}$ on $R_{\{717\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$) *i.e.* for $\alpha = 35.35°$ and $\gamma = 55.08°$. (b) The curves representing intersections of limiting surfaces $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit}$ given by equation (6) with the $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit} = 1$ plane. Curve 1 corresponds to the surface shown in Figure 5a obtained for concanavalin A crystal. The shaded region means that for relative growth rates $R_{\{717\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$ lying in this region the {717} face of this crystal develops its size although it grows faster than both the neighbouring faces. The angles α and γ are respectively equal to: 35.35° and 55.08° for curve 1, 25.35° and 45.08° for curve 2, 45.35° and 65.08° for curve 3.

and $R_\mathrm{A}/R_\mathrm{D} = R_{\{717\}}/R_{\{001\}}$ shown in Figure 5a. Additionally, the plane $R_\mathrm{A}/R_\mathrm{A}^\mathrm{crit} = R_{\{717\}}/R_{\{717\}}^\mathrm{crit} = 1$ is shown. The curve 1 is the intersection line of this plane with the limiting surface given by equation (6) applied to concanavalin A crystal. From this figure it is seen that depending on the values of the relative growth rates $R_{\{717\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$ the ratio $R_{\{717\}}/R_{\{717\}}^\mathrm{crit}$ takes values smaller than (below the curve 1), equal to (on the curve 1) or greater than (above the curve 1) unity. This means that these relative growth rates influence the behaviour of the {717} face and depending on their values this face increases, preserves or decreases its size, respectively. We can also notice that the ratio $R_{\{717\}}/R^{\rm crit}_{\{717\}}$ takes values smaller than unity even for relative growth rates $R_{\{717\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$ greater than unity. This indicates that the {717} face increases its size even when it grows faster than both the neighbouring faces {100} and {001}. It is easier to notice this looking at Figure 5b. This figure shows the curves representing intersections of limiting surfaces $R_{\rm A}/R^{\rm crit}_{\rm A}$ given by equation (6) with $R_{\rm A}/R^{\rm crit}_{\rm A} = 1$ plane for various values of the angles α and γ. Curve 1 corresponds to the surface shown in Figure 5a obtained for concanavalin A crystal, *i.e.* for $\alpha = 35.35°$ and $\gamma = 55.08°$. The shaded region means that for relative growth rates $R_{\{717\}}/R_{\{100\}}$ and $R_{\{717\}}/R_{\{001\}}$ lying in this region, the high-index {717} face of this crystal develops its size even though it grows faster than both the neighbouring faces {100} and {001}. The range of this region of the relative growth rates, for which such a phenomenon occurs, depends on the crystallographic structure of a given crystal which is represented by the interfacial angles α and γ. To prove this let us concentrate for a while on the curve 2 which is obtained for $\alpha = 25.35°$ and $\gamma = 45.08°$. It is seen that the region of relative growth rates for which the given face with these interfacial angles would increase in spite of its growing faster than the neighbouring faces is much smaller in comparison with that for {717} face. On the other hand, there exist faces with such interfacial angles for which the range of the region of the appropriate relative growth rates is very wide. For example, curve 3 is obtained for $\alpha = 45.35°$ and $\gamma = 65.08°$, and it is seen that the face with these angles would develop its size even if it grew four times faster than the neighbouring face D ($R_{\rm A}/R_{\rm D} = 4$). It should be pointed out that the values of angles α and γ for which the curves 2 and 3 are obtained are assumed theoretically and they are not connected with concanavalin A crystal.

From the above it follows that the phenomenon of developing of sizes of crystal faces growing faster than the neighbouring faces depends, on one hand, on the relative growth rates, but on the other hand, on the crystallographic structure of crystal. However, for given relative growth rates the existence of such an effect depends only on crystallographic structure of a given crystal represented by appropriate interfacial angles. There exist faces with such interfacial angles, that they increase in size even if they grow much faster than the neighbouring faces. High-index faces are often those with such interfacial angles. Therefore, such a crystallographic structure of high-index faces may be one of the possible explanations of growth and existence of these faces in crystal morphologies. It should be pointed out that this is purely geometrical effect, not connected with energetic influences. On the other hand it should be emphasised that in reference [12], the authors described the $\{n1n\}$ faces of concanavalin A crystals as flat faces. Taking this into account and taking into account the theoretical background briefly presented in Introduction, it is possible to draw a conclusion that also high-index faces could grow with a layer mechanism with well defined orientation.

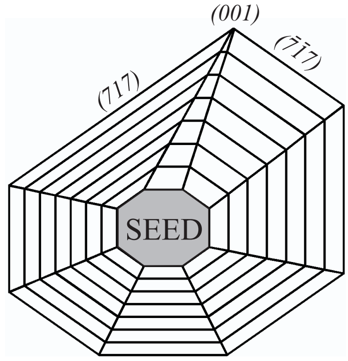


Fig. 6. The cross-section of concanavalin A crystal illustrating the disappearance of low-index (001) face.

3.3 The behaviour of low-index faces on the example of {001} face of concanavalin A crystal

Let us take a closer look at Figure 6 which illustrates an unusual behaviour of the (001) face, one of the faces from the set {001} of concanavalin A crystal. This face has two neighbouring faces from the set {717}, namely (717) and ($\bar{7}\bar{1}7$) faces (Fig. 6). The low-index face (001) grows here with the following relative growth rates $R_{(001)}/R_{(717)} = 2.0$ and $R_{(001)}/R_{(\bar{7}\bar{1}7)} = 1.0$. In other words, the (001) face grows faster than the (717) face and equally fast as the ($\bar{7}\bar{1}7$) face. We can see in Figure 6 that, unexpectedly, the low-index (001) face decreases and finally disappears, while both the neighbouring high-index faces ($\bar{7}\bar{1}7$) and (717) develop their sizes. This unusual phenomenon is also determined by the crystallographic structure of the crystal. As it is derived in reference [21], such a phenomenon occurs only when $2\alpha + \gamma < \pi$ – the face A may disappear at growth rate smaller than $R_{\rm D}$; or $2\gamma + \alpha < \pi$ – the face A may disappear at growth rate smaller than $R_{\rm B}$. Additionally, the relative growth rate $R_{\rm B}/R_{\rm D}$ must satisfy a given condition which is also determined by the angles α and γ [21]. From this it follows that unexpected behaviour of not only high-index faces but also low-index faces may be explained based on crystallographic structure of a given crystal.

4 Conclusions

From the above analysis we conclude that the existence and developing of size of high-index faces may be explained based on crystallographic structure of a given crystal. Usually, high-index faces, which appear between low-index faces, produce such interfacial angles that even growing faster than the neighbouring faces, they need not decrease and, as a result, disappear from crystal morphology but contrariwise, they may increase in size. Additionally, low-index faces, at particular crystallographic structure of a given crystal may disappear growing more slowly than or equally fast as one of the neighbouring faces. Both these facts determine the basis for one of the possible explanations of the growth and existence of high-index faces in crystal morphologies. It should be pointed out that these conclusions are drawn from purely crystallographic arguments, not the energetic ones.

In order to illustrate the proposed ideas, they were applied to concanavalin A crystal in which the high-index {717} faces are observed. The crystallographic structure of this crystal is such that this high-index face increases in size even if it grows faster than the neighbouring faces. Additionally, it is shown that the low-index {001} face decreases its size growing equally fast as one of the neighbouring faces. This effect is also determined by the crystallographic structure of concanavalin A crystal. Additionally, as the $\{n1n\}$ faces (n ranged from 7 to 11) of this crystal were found to be macroscopically flat [12], it is possible that high-index faces grow by a layer mechanism. This is an open challenge for the theory, because, in principle, high-index faces are supposed to grow as rough rounded off faces.

Appendix A

Equation (2) deals with the set {717} and its size changes. It was obtained by substituting $R^{\rm crit}_{\{717\}}$ as $R^{\rm crit}_{\rm A}$, $R_{\{100\}}$ as $R_{\rm B}$ and $R_{\{001\}}$ as $R_{\rm D}$ into equation (1) and taking the angles $\alpha = 55.08°$ and $\gamma = 35.35°$ (*cf.* Fig. 2b). It is seen that the $R^{\rm crit}_{\{717\}}/R_{\{100\}}$ ratio is a linear function of the relative growth rate $R_{\{001\}}/R_{\{100\}}$, which may change with growth conditions.

In order to precisely analyse the changes in size of the {001} face, we should consider the relative growth rate $R^{\rm crit}_{\{001\}}/R_{\{100\}}$. In this case $R_{\rm B} = R_{\rm D} = R_{\{717\}}$ and the angles $\alpha = \gamma = 35.35°$. Substituting these data into equation (1) and dividing by $R_{\{100\}}$, we obtain that the critical relative growth rate $R^{\rm crit}_{\{001\}}/R_{\{100\}}$ equals to:

$$\frac{R^{\rm crit}_{\{001\}}}{R_{\{100\}}} = 1.23\frac{R_{\{717\}}}{R_{\{100\}}}\,. \tag{A1}$$

It is seen that the $R^{\rm crit}_{\{001\}}/R_{\{100\}}$ ratio is a linear function of the relative growth rate $R_{\{717\}}/R_{\{100\}}$, which may change with growth conditions.

Finally, let us take a closer look at the set {100}. In this case $R_{\rm B} = R_{\rm D} = R_{\{717\}}$ and the angles $\alpha = \gamma = 55.08°$ (*cf.* Fig. 2b). Substituting these data into equation (1) and dividing by $R_{\{717\}}$ we obtain that:

$$\frac{R^{\rm crit}_{\{100\}}}{R_{\{717\}}} = 1.75. \tag{A2}$$

The ratio $R^{\rm crit}_{\{100\}}/R_{\{717\}}$ is constant and independent of the growth rates of neighbouring faces.

In this way we have found three dependences given by equations (2, A1) and (A2), which deal with the size changes of the sets {717}, {001} and {100}, respectively. The values of the critical relative growth rates estimated on the basis of these equations mean that for the relative growth rates $R_{\{717\}}/R_{\{100\}}$, $R_{\{001\}}/R_{\{100\}}$ and $R_{\{100\}}/R_{\{717\}}$ equal to the critical ones, the sizes of, respectively, the sets {717}, {001} and {100}, remain the same during the further growth process. The growth with the relative growth rates $R_{\{717\}}/R_{\{100\}}$, $R_{\{001\}}/R_{\{100\}}$ and $R_{\{100\}}/R_{\{717\}}$ smaller (greater) than critical leads to continuous increase (decrease) in the size of the sets {717}, {001} and {100}, respectively.

In order to consider all these dependence in one graph, it is necessary to rearrange these equalities, aiming to have the same variables in all equations. It is very convenient to consider the dependence of $R_{\{717\}}/R_{\{100\}}$ on variable $R_{\{001\}}/R_{\{100\}}$ (*cf.* Eq. (2)). To achieve this, we have to rearrange two equalities, namely equations (A1, A2), while equation (2) remains unchanged. After rearranging the equation (A1) takes form of equation (3) and transforming equation (A2) properly, we obtain equation (4).

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