Correlation Between Crystal Structure, Relative Growth Rates and Evolution of Crystal Surfaces

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According to most crystal growth theories, the "as grown" crystal morphology is dominated by the slow-growing faces and the fast-growing faces may "grow out" and not be represented in the final crystal habit. In this paper a brief survey is given of the recently developed correlation between the evolution of both fast- and slow-growing surfaces, their relative growth rates, and the crystallographic structure of crystal. It is shown that even the fast-growing faces may increase their sizes. On the other hand, the slow-growing faces may decrease and, in consequence, disappear from crystal morphology. Such a behaviour of slow- and fast-growing surfaces influences the growth and evolution of both low- and high-index faces.

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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 ones growing most slowly. 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

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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. 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 play 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 HP 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 faces of crystals that grow below their roughening temperature are flat faces with well-defined hkl orientation. They grow by a layer mechanism, like spiral growth or two-dimensional nucleation. The faces, which are not parallel to a connected net, have a roughening temperature equal to 0 K and, therefore, they always grow as rough rounded off faces.

According to most of these theories the "as-grown" crystal morphology is dominated by the slow-growing surfaces and the fast-growing faces may "grow out" and not be represented in the final crystal habit. Other theories are not concerned with the occurrence of fast-growing faces in final crystal morphologies. Therefore, the aim of this paper is a brief survey of recent developments in the field of evolution of slow- and fast-growing surfaces, focusing attention on the crystallographic structure of crystal and relative growth rates.

2. Method of analysis

The habit of a single crystal changes during the growth process, since relative growth rates of the faces concerned vary owing to fluctuation in growth parameters.

Behaviour of a given face during the growth process is quite difficult to analyse on the basis of external crystal morphology. However, it can be investigated on the basis of internal morphology, because all changes are "recorded" in the crystal in a form of growth banding in respective growth sectors and growth sector boundaries, i.e. in a form of internal morphology [12]. The internal morphology is revealed in crystal cross-sections.

Figure 1 illustrates a cross-section of a hypothetical crystal with growth bands (GB), growth sectors (GS), and growth sector boundaries (GSB). For crystals grown in nature and, in most cases, for crystals obtained artificially in laboratories, growth bands appear as a result of changes of growth conditions, during the growth process in unknown time intervals. In such a case, it is possible to investigate the changes in crystal morphology depending on relative growth rates. Straight boundaries between adjacent growth sectors (cf. Fig. 1) 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 were not constant.

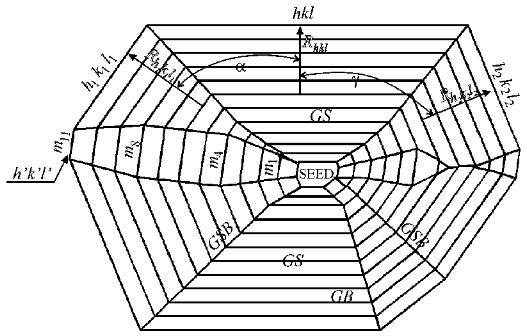

Fig. 1. Exemplary cross-section of a hypothetical 3D crystal with the considered hkl face and its neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces; $R_{hkl}, R_{h_1k_1l_1}, R_{h_2k_2l_2}$ — the normal growth rates of the $hkl, h_1k_1l_1$ and $h_2k_2l_2$ faces, respectively, α, γ — the interfacial angles, GB — growth bands, GS — growth sectors, GSB — growth sector boundaries, m_1 to m_{11} — consecutive growth bands on the $h'k'l'$ face growth sector.

Thus, from the above it results that for crystals whose growth process cannot be observed *in situ*, e.g. natural crystals or crystals synthesised by high temperature solution or hydrothermal solution methods, the internal morphology revealed in crystal cross-section gives information on the growth process and the evolution of individual faces. For this reason, in order to study the effect of crystal geometry on the growth behaviour of faces, both slow- and fast-growing, we use the idea of the critical relative growth rate $R_{hkl}/R_{hkl}^{\text{crit}}$. The critical relative growth rate $R_{hkl}/R_{hkl}^{\text{crit}}$ is expressed by the formula [13, 14]:

$$\frac{R_{hkl}}{R_{hkl}^{\text{crit}}} = \frac{\sin(\alpha+\gamma)}{\frac{\sin\gamma}{R_{hkl}/R_{h_1k_1l_1}} + \frac{\sin\alpha}{R_{hkl}/R_{h_2k_2l_2}}}, \tag{1}$$

where $R_{h_1k_1l_1}$ and $R_{h_2k_2l_2}$ are the normal growth rates of the $h_1k_1l_1$ and $h_2k_2l_2$ faces, respectively. The $h_1k_1l_1$ and $h_2k_2l_2$ faces are the neighbouring faces of the hkl face (Fig. 1). The angles α and γ are the interfacial angles defined in Fig. 1. The detailed explanation how this equation was derived is given in Appendix A. It is seen that the ratio $R_{hkl}/R_{hkl}^{\text{crit}}$ is a function of the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$ which may take different values depending on growth environment. Aditionally, the ratio $R_{hkl}/R_{hkl}^{\text{crit}}$ is a function of the interfacial angles α and γ representing the crystal geometry. The physical meaning of the ratio $R_{hkl}/R_{hkl}^{\text{crit}}$ is as follows [13, 14]:

- For $R_{hkl}/R_{hkl}^{\text{crit}} < 1$, the size of the hkl face increases. If the hkl face does not exist in the habit, it appears and develops its size. This may be observed on the example of the $h'k'l'$ face visible in Fig. 1. Here, the ratio $R_{h'k'l'}/R_{h'k'l'}^{\text{crit}}$, beginning from the seed up to the m_4 growth band, is smaller than unity and, therefore, this face increases its initial size.
- For $R_{hkl}/R_{hkl}^{\text{crit}} = 1$, the size of the hkl face is preserved. If the initial size of this face is equal to zero, the zero size is preserved, i.e. this face does not appear in the habit. In the case of the $h'k'l'$ face shown in Fig. 1, the ratio $R_{h'k'l'}/R_{h'k'l'}^{\text{crit}}$ is equal to unity, beginning from m_4 to m_8 growth band. This is why this face does not change its size at this stage of growth.
- For $R_{hkl}/R_{hkl}^{\text{crit}} > 1$, the size of the hkl face decreases. This may lead, in consequence, to its disappearance. If the face does not exist in the habit, it still does not appear. In the case of the exemplary $h'k'l'$ face (Fig. 1) the ratio $R_{h'k'l'}/R_{h'k'l'}^{\text{crit}}$ changes its value, becoming greater than unity beginning from m_8 growth band. This leads to the decreasing in size of the $h'k'l'$ face.

In this paper, we focus our attention on the influence of crystal geometry, represented by the interfacial angles α and γ, on the growth behaviour of crystal surfaces, both slow- and fast-growing. In order to study such an influence of crystal geometry we use the idea of the critical relative growth rate and consider the ratio $R_{hkl}/R_{hkl}^{\text{crit}}$ for different values of the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$. Our analysis is restricted to the interfacial angles satisfying the condition $\alpha+\gamma<\pi$, because only for such interfacial angles, a given face may increase, preserve, or decrease its initial size. The condition $\alpha+\gamma=\pi$ corresponds to the hkl face situated between two parallel faces. In such a case, the hkl face never disappears. As follows from Eq. (1), for $\alpha+\gamma=\pi$ the ratio $R_{hkl}/R_{hkl}^{\text{crit}}$ tends to zero. For $\alpha+\gamma>\pi$ (for example tetrahedral habit), a given hkl face can only increase. The ratio $R_{hkl}/R_{hkl}^{\text{crit}}$ starts to take negative values and the idea of the critical relative growth rate and, at the same time, Eq. (1) loses its physical sense [13, 14].

3. Results and discussion

3.1. Fast-growing surfaces

According to the knowledge hitherto existing, we should expect the *hkl* face to decrease its size and, in consequence, to disappear if it grows faster than both neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces. Let us analyse this case based on Fig. 2a. This figure shows the dependence of the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ (Eq. (1)) on the interfacial angles α and γ, for different values of the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$, but always satisfying the conditions $R_{hkl}/R_{h_1k_1l_1} > 1$ and $R_{hkl}/R_{h_2k_2l_2} > 1$ (see caption of Fig. 2). This means that the *hkl* face is the fast-growing face.

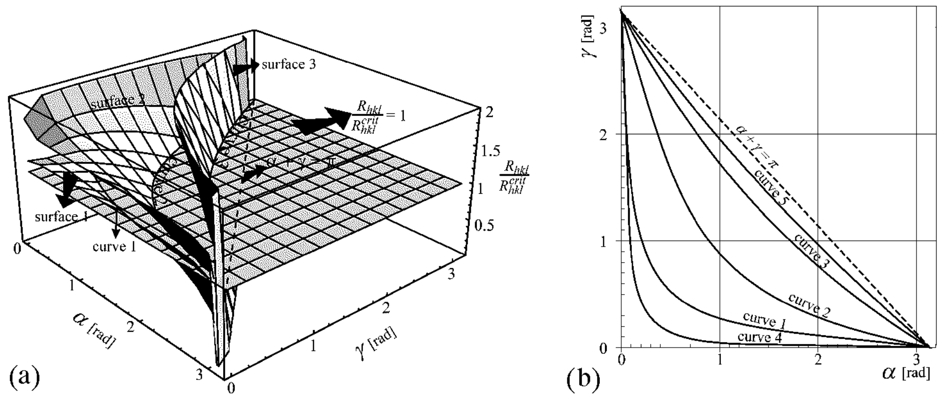

Fig. 2. The dependence of the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ on the angles α and γ (Eq. (1)): (a) 3D graph — for different values of the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$ satisfying the conditions $R_{hkl}/R_{h_1k_1l_1} > 1$ and $R_{hkl}/R_{h_2k_2l_2} > 1$; (b) 2D graph — the curves representing intersections of $R_{hkl}/R_{hkl}^{\rm crit}$ surfaces given by Eq. (1) with $R_{hkl}/R_{hkl}^{\rm crit} = 1$ plane. Curves 1, 2 and 3 correspond to surfaces 1, 2 and 3 shown in Fig. 2a. The relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$ are respectively equal to: 1.10 and 1.20 for surface 1/curve 1; 2.00 and 1.50 for surface 2/curve 2; 4.00 and 5.00 for surface 3/curve 3; 1.05 and 1.03 for curve 4; 9.00 and 11.00 for curve 5. For $\alpha + \gamma > \pi$, Eq. (1) loses its physical meaning.

Let us consider the surface 2 (Fig. 2a) which corresponds to the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$ equal to 2.00 and 1.50, respectively. It may be noticed that if one of the interfacial angles α or γ, or both these interfacial angles, take quite small values, the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ is greater than unity. This means that for such interfacial angles the *hkl* face decreases its size, in agreement with our expectations. However, for the interfacial angles α and γ lying on the curve 2 (cf. Figs. 2a and b — this curve is the intersection line of the surface 2 given by Eq. (1) for $R_{hkl}/R_{h_1k_1l_1} = 2.00$ and $R_{hkl}/R_{h_2k_2l_2} = 1.50$, with the plane

$R_{hkl}/R_{hkl}^{\rm crit} = 1$), the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ is equal to unity. Therefore, for the interfacial angles α and γ lying on the curve 2 the hkl face preserves its size. Further, the ratio $R_{hkl}/R_{hkl}^{\rm crit}$, presented by surface 2, takes values smaller than unity — for appropriate values of the angles α and γ, the considered hkl face increases its initial size. It is easier to understand this situation analysing the dependence of the angle γ on the angle α in 2D graph presented in Fig. 2b. Each of the curves is obtained for different relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$, but the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ equals unity for all the curves. In other words, the curves are the intersection lines of the surfaces presented in Fig. 2a with the plane $R_{hkl}/R_{hkl}^{\rm crit} = 1$. Some of these intersection lines are visible in Fig. 2a (curves 1, 2 and 3), however, Fig. 2b is clearer and two additional curves, namely 4 and 5, are shown. For values of the angles lying below a given curve, the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ is greater than 1 and, therefore the hkl face decreases its size, for the angles lying exactly on a given curve, the size of the hkl face is preserved ($R_{hkl}/R_{hkl}^{\rm crit} = 1$) and for the angles lying above a given curve, the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ is smaller than unity and the size of the hkl face increases.

If the hkl face grows faster than one of the neighbouring faces and, at the same time, as fast as the other neighbouring face, the hkl face, similarly as in the previous case, may behave in three different ways, depending on the values of the interfacial angles α and γ. It may decrease, preserve, or increase its initial size. In the case of the hkl face growing with the same growth rate as the neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces ($R_{hkl}/R_{h_1k_1l_1} = 1.00$ and $R_{hkl}/R_{h_2k_2l_2} = 1.00$), the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ given by Eq. (1), does not exceed unity. This means that the hkl face may behave in one way only — it increases its size [14].

From the above considerations it results that at given relative growth rates $R_{hkl}/R_{h_1k_1l_1} > 1$ and $R_{hkl}/R_{h_2k_2l_2} > 1$, the fast-growing hkl face behaves in different ways depending on the geometry of crystal that is expressed by interfacial angles α and γ [13, 14]. The fast-growing hkl face may decrease or preserve its initial size or, at particular geometry, it may enlarge its size growing much faster than the neighbouring faces [14]. The faster the hkl face grows (the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$ increase) the greater values the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ takes and the surface corresponding to this ratio becomes almost vertical (Fig. 2a — surface 3). Simultaneously, the range of interfacial angles α and γ, for which the fast-growing hkl face increases its size, decreases — cf. curve 5 in Fig. 2b. For $\alpha + \gamma > \pi$ the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ becomes smaller than zero, and Eq. (1) loses its physical meaning.

3.2. Slow-growing surfaces

First, let us concentrate on the case when a given hkl face grows more slowly than both neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces. This case is illustrated in Fig. 3a showing the dependence given by Eq. (1) for $R_{hkl}/R_{h_1k_1l_1} = 0.50$ and $R_{hkl}/R_{h_2k_2l_2} = 0.30$. From this figure it is seen that if the hkl face grows more

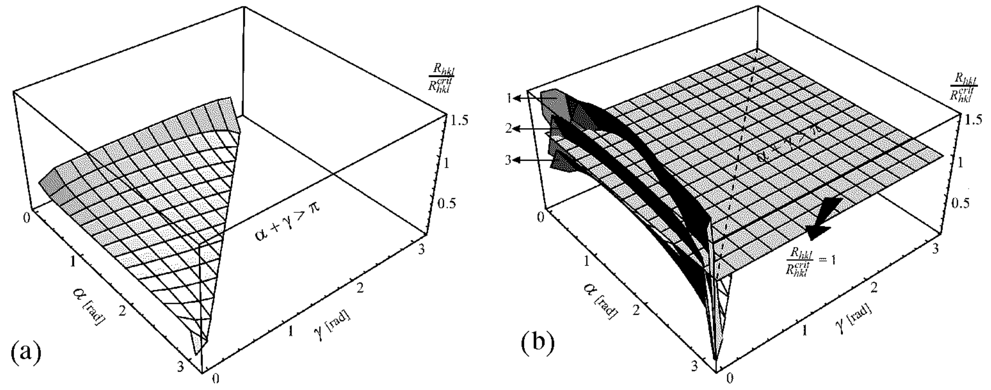

Fig. 3. The ratio $R_{hkl}/R_{hkl}^{\rm crit}$, given by Eq. (1), depending on the angles α and γ in a case when: (a) the hkl face grows more slowly than both neighbouring faces: $R_{hkl}/R_{h_1k_1l_1} = 0.5$, $R_{hkl}/R_{h_2k_2l_2} = 0.3$; (b) the hkl face grows more slowly than one neighbouring face — $h_1k_1l_1$ face: surface 1 for $R_{hkl}/R_{h_1k_1l_1} = 0.7$, $R_{hkl}/R_{h_2k_2l_2} = 5.0$, surface 2 for $R_{hkl}/R_{h_1k_1l_1} = 0.5$, $R_{hkl}/R_{h_2k_2l_2} = 1.5$, surface 3 for $R_{hkl}/R_{h_1k_1l_1} = 0.4$, $R_{hkl}/R_{h_2k_2l_2} = 1.0$. For $\alpha + \gamma > \pi$, Eq. (1) loses its physical meaning.

slowly than both neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces, the ratio $R_{hkl}/R_{hkl}^{\rm crit}$ does not exceed unity. This means that, in such a case, the hkl face may only increase its size [13]. The preservation of the initial size or the disappearance of the hkl face is not possible. This situation changes when the hkl face grows more slowly than only one of the neighbouring faces: $h_1k_1l_1$ or $h_2k_2l_2$. This case is illustrated in Fig. 3b presenting the dependence given by Eq. (1) for different values of relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$ (the values are given in the caption of this figure). Let us note that two of the three surfaces (surfaces 1 and 2), obtained for given values of relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$, exceed unity and one of the surfaces (surface 3), for other values of the relative growth rates, does not reach unity. Therefore, we conclude that for some values of the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$ there is a possibility of decreasing and, in consequence, of disappearing of a given face even if it grows more slowly than one of the neighbouring faces. A detailed analysis shows that such a phenomenon may occur only when the relative growth rate $R_{h_1k_1l_1}/R_{h_2k_2l_2}$ satisfies one of the following conditions [13]:

$$\frac{R_{h_1k_1l_1}}{R_{h_2k_2l_2}} < \frac{\sin(\alpha+\gamma)-\sin\alpha}{\sin\gamma}, \tag{2a}$$

$$\frac{R_{h_1k_1l_1}}{R_{h_2k_2l_2}} > \frac{\sin\alpha}{\sin(\alpha+\gamma)-\sin\gamma}. \tag{2b}$$

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

The above inequalities cannot be satisfied simultaneously. Equation (2a) is satisfied for $R_{h_2k_2l_2} > R_{h_1k_1l_1}$, while Eq. (2b) for $R_{h_1k_1l_1} > R_{h_2k_2l_2}$. Consequently, the disappearance of the considered hkl face at the growth rate simultaneously smaller than the growth rates of both neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces is impossible. Therefore, we conclude that, in the case of $R_{h_1k_1l_1} \neq R_{h_2k_2l_2}$, the considered hkl face may disappear from the habit even growing more slowly than the faster-growing one of the two neighbouring $h_1k_1l_1$ or $h_2k_2l_2$ faces. Such a phenomenon is possible only for particular geometry of a given hkl face. The interfacial angles α and γ characterising such a geometry must satisfy one of the conditions: $2\alpha + \gamma < \pi$ — the hkl face may disappear at growth rate smaller than $R_{h_2k_2l_2}$; or $2\gamma + \alpha < \pi$ — the hkl face may disappear at growth rate smaller than $R_{h_1k_1l_1}$ [13].

From the above analysis it can be found that at given relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$, the hkl face behaves in different ways depending on the geometry of crystal, expressed by interfacial angles α and γ. In particular, it decreases its size even if it grows more slowly than one of the neighbouring faces.

4. Verification of the theoretical model

In order to find out whether the proposed theoretical model is suitable for real problems of crystal growth, we consider two crystals: a lecithin protein concanavalin A crystal and potassium bichromate (KBC) crystal. In Sec. 4.1, the growth behaviour of various faces of both these crystals is analysed using computer simulation. In Sec. 4.2, the experimental verification for KBC crystal is presented.

4.1. Exemplary analysis by computation

The exemplary analysis of growth behaviour of concanavalin A and potassium bichromate crystals is made with the aid of computer program SHAPE (version 6.0 professional [15]). SHAPE is a crystal drawing program whose basic concepts were published in Ref. [16]. It uses the classical Wulff plot of the equilibrium form. In the present work this program is used as a graphic tool to illustrate the cross-sections of the crystals under considerations.

4.1.1. Concanavalin A crystal

The unusual behaviour of both slow- and fast-growing faces may influence the growth of high-index faces. Let us consider 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. However, in Ref. [19], the authors suggest that the high-index $\{n1n\}$ faces appear, where the value n ranged from 7 to 11. Moreover, the authors found the $\{n1n\}$ faces of concanavalin A crystal to be macroscopically flat, in spite of their high in-

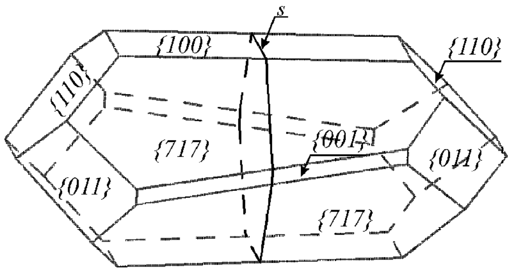

Fig. 4. The theoretically assumed growth morphology of concanavalin A crystal with the considered high-index {717} face. The *s* line indicates the position of the cross-section presented in Fig. 5.

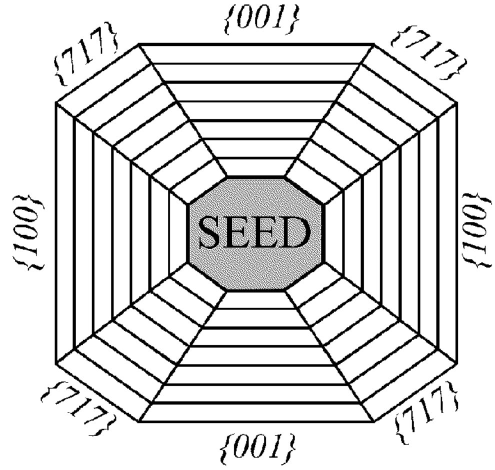

Fig. 5. The exemplary cross-section of concanavalin A crystal morphology which illustrates increasing in size of fast-growing high-index {717} face.

dexes. For this reason, this crystal is very interesting to investigate the growth behaviour of high-index faces and was therefore chosen as a modelling crystal. For the purpose of this article we consider, besides low-index faces, also particular high-index {717} faces — Fig. 4. All faces shown in Fig. 4 were experimentally observed and reported [18, 19]. The cross-section of concanavalin A crystal shown in Fig. 5 results from cleaving of the crystal from Fig. 4 along *s* line. As it is seen in Fig. 5, the high-index {717} faces have two neighbouring sets of faces: {100} and {001}. Here, the {717} face is the fastest growing face. The values of the relative growth rates, taken for the modelling computation are equal to: $R_{\{717\}}/R_{\{100\}} = R_{\{717\}}/R_{\{001\}} = 1.20$. As a result of simulation the {717} face increases its size — Fig. 5. The unusual behaviour of this face may be explained by the specific values of the interfacial angles α and γ [20]. The crystallographic structure of high-index faces, characterised by interfacial angles, may be one of the possible reasons of growth and existence of these faces in crystal morphologies. This is purely geometrical effect, without taking into account surface free energy. However, the $\{n1n\}$ faces were reported as flat faces [19]. Thus, the theoretical background briefly presented in Introduction reveals that also the high-index faces could grow with a layer mechanism with well-defined *hkl* orientation.

4.1.2. KBC crystal

Potassium bichromate ($K_2Cr_2O_7$ — KBC) crystal belongs to $\bar{1}$ point group with the following unit cell parameters: $a = 7.445$ Å, $b = 7.376$ Å, $c = 13.367$ Å, $\alpha = 97.96°$, $\beta = 96.21°$, $\gamma = 90.75°$ [21]. Let us consider the cross-section of KBC crystal shown in Fig. 6a. For this exemplary growth history the constant relative growth rates were chosen as shown in Table. Additionally, this Table gives the values of the ratio $R_{hkl}/R_{hkl}^{\text{crit}}$, calculated on the basis of Eq. (1). In KBC crystal, the (001) face situated between the (011) and $(0\bar{1}1)$ faces ($\alpha \angle (001)/(011) = 54.90°$, $\gamma \angle (001)/(0\bar{1}1) = 67.29°$), is usually the biggest face and, therefore, so far it has been considered as the slowest-growing face. However, in Fig. 6a, it is seen that this face increases in size growing either more slowly or faster than the neighbouring (011) or $(0\bar{1}1)$ faces. From the beginning of growth process up to m_5 growth band, the relative growth rates $R_{hkl}/R_{h_1k_1l_1} = R_{(001)}/R_{(011)}$ and $R_{hkl}/R_{h_2k_2l_2} = R_{(001)}/R_{(0\bar{1}1)}$ are smaller than unity (Table). This means that the (001) face grows more slowly than the neighbouring faces and, in accordance with our expectations, the growth sector associated with this face is widening. Thus, the (001) face increases. Beginning from m_5 growth band, the relative growth rates $R_{(001)}/R_{(011)}$ and $R_{(001)}/R_{(0\bar{1}1)}$ are greater than unity (Table), thus, the (001) face is the fast-growing face but, in spite of this, it still increases its size. Possible reasons of variations of relative growth rates during real

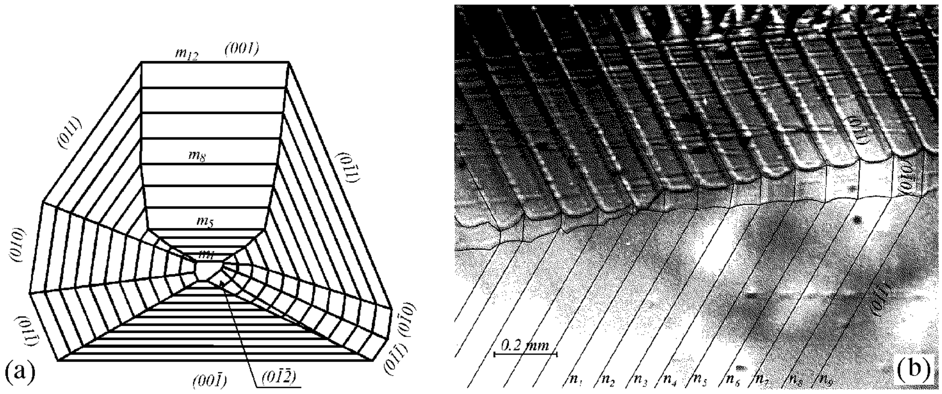

Fig. 6. Cross-section of KBC crystal (a) obtained by computer simulation, the numeration m_1 to m_{12} denotes the consecutive growth bands, (b) grown from solution; the numeration n_1 to n_9 denotes the consecutive induced striations. Plane of observation $(\bar{1}00)$.

crystal growth process are, for example, impurities or fluctuations in growth conditions. It is seen from Table that the values of the ratio $R_{(001)}/R^{\text{crit}}_{(001)}$ are smaller than unity, and accordingly the (001) face increases in size. It confirms that a given face may increase in size even though it grows faster than the neighbouring faces.

Further, let us focus on $(0\bar{1}\bar{2})$ face ($\alpha\ \angle\ (0\bar{1}\bar{2})/(0\bar{1}\bar{1}) = 16.54°$ and $\gamma\ \angle\ (0\bar{1}\bar{2})/(00\bar{1}) = 38.36°$). Beginning from m_1 growth band (in Fig. 6a the numeration of growth bands is not shown in the $(0\bar{1}\bar{2})$ face growth sector), the $(0\bar{1}\bar{2})$ face grows faster than the $(00\bar{1})$ face and, at the same time, more slowly than or equally fast as $(0\bar{1}\bar{1})$ face (Table). As a result, the $(0\bar{1}\bar{2})$ face decreases its size and, in consequence, disappears, although it grows not faster than the neighbouring $(0\bar{1}\bar{1})$ face.

4.2. Experimental verification

Figure 6b illustrates cross-section of KBC crystal grown from solution by the method of decreasing temperature. The growth bands seen in this figure were induced artificially by changing the hydrodynamic conditions in equal and known time intervals. Such growth bands, which are induced artificially, are called induced striations. Etching the cleavage plane in HCOOH revealed the induced striations seen in Fig. 6b. There are some faces for which the induced striations are visible very well, but for some other faces they are not visible at all, for instance, the induced striations are not visible at the growth sector of the $(0\bar{1}\bar{1})$ face. Therefore, in order to improve the legibility, the lines indicating induced striations and growth sector boundaries are added to the figure.

Let us analyse the growth behaviour of the $(0\bar{1}0)$ face shown in Fig. 6b. This face is situated between $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$ faces and the interfacial angles

TABLE

The relative growth rates: TA — theoretically assumed, used to obtain the cross-section of KBC crystal shown in Fig. 6a, CA — calculated on the basis of Eq. (1). Symbol ↑ or ↓ means that the given face increases or decreases its size between appropriate growth bands presented in Fig. 6a.

Growth bands	Relative growth rate		
	TA	TA	CA
	$R_{hkl}/R_{h_1k_1l_1}$	$R_{hkl}/R_{h_2k_2l_2}$	$R_{hkl}/R_{hkl}^{\mathrm{crit}}$
(001) face			
	$R_{(001)}/R_{(011)}$	$R_{(001)}/R_{(0\bar{1}1)}$	$R_{(001)}/R_{(001)}^{\mathrm{crit}}$
up to m_1	0.65	0.54	0.29 ↑
m_1-m_3	0.50	0.56	0.26 ↑
m_3-m_5	0.60	0.71	0.31 ↑
m_5-m_8	1.50	1.76	0.78 ↑
m_8-m_{12}	1.75	2.06	0.92 ↑
$(0\bar{1}\bar{2})$ face			
	$R_{(0\bar{1}\bar{2})}/R_{(0\bar{1}\bar{1})}$	$R_{(0\bar{1}\bar{2})}/R_{(00\bar{1})}$	$R_{(0\bar{1}\bar{2})}/R_{(0\bar{1}\bar{2})}^{\mathrm{crit}}$
up to m_1^*	0.71	0.71	0.65 ↑
m_1-m_2	1.00	2.00	1.07 ↓
m_2-m_3	1.00	2.00	1.07 ↓
m_3-m_{12}	0.93	2.10	1.02 ↓

*the numeration of growth bands on $(0\bar{1}\bar{2})$ face growth sector is not shown in Fig. 6a.

α ($\angle$ $(0\bar{1}0)/(0\bar{1}1)$) and γ ($\angle$ $(0\bar{1}0)/(0\bar{1}\bar{1})$) are equal to 30.80° and 27.01°, respectively. It is seen that the size of the $(0\bar{1}0)$ face fluctuates a little, but starting from induced striation denoted by n_1 (Fig. 6b), it increases. The detailed analysis [14] shows that the $(0\bar{1}0)$ face is fast-growing face, i.e. it grows faster than both neighbouring $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$ faces. In spite of this it enlarges.

5. Conclusions

The main results of this study may be summarised as follows:

- The behaviour of a given face during the growth process depends not only on the relative growth rates which may vary with growth conditions, but also on the geometry of a given face represented by appropriate interfacial angles.
- If the hkl face, situated between two neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces, is a fast-growing face ($R_{hkl}/R_{h_1k_1l_1} > 1$ and $R_{hkl}/R_{h_2k_2l_2} > 1$), there are three possible ways of behaviour of the hkl face. It may decrease, preserve,

or, for a given range of interfacial angles α and γ, it may increase its size even if it grows faster than the $h_1k_1l_1$ and $h_2k_2l_2$ faces. The width of this range of interfacial angles, for which such a phenomenon may occur, depends on the values of the relative growth rates $R_{hkl}/R_{h_1k_1l_1}$ and $R_{hkl}/R_{h_2k_2l_2}$. The greater these values (the faster the hkl face grows), the smaller the range of these interfacial angles.

- If the hkl face grows faster than one of the neighbouring faces and, at the same time, as fast as the other neighbouring face, the hkl face may decrease, preserve or increase its initial size.
- If the hkl face grows as fast as both neighbouring $h_1k_1l_1$ and $h_2k_2l_2$ faces, the hkl face may only increase its initial size.
- If the hkl face grows more slowly than one of the neighbouring $h_1k_1l_1$ or $h_2k_2l_2$ faces it may disappear from the crystal habit. However, $R_{h_1k_1l_1}/R_{h_2k_2l_2}$ must satisfy one of the conditions given by Eq. (2a) or Eq. (2b). This means that the interfacial angles α and γ that characterise crystal geometry, must satisfy one of the conditions: $2\alpha + \gamma < \pi$ or $2\gamma + \alpha < \pi$. These conditions correspond to the hkl face disappearance at growth rate smaller than the growth rate of the neighbouring $h_2k_2l_2$ face or $h_1k_1l_1$ face, respectively. The geometry shows that the hkl face never disappears growing more slowly than both neighbouring $h_1k_1l_1$ and $h_21k_2l_2$ faces.
- On the basis of the verification performed for concanavalin A crystal we conclude that the existence and development of the size of high-index faces may be explained based on crystallographic structure of a given crystal. Usually, the high-index faces, which appear between low-index faces, produce such interfacial angles that even growing faster than the neighbouring faces, do not disappear from crystal morphology. This fact determines the basis for one of the possible explanations of the growth and existence of high-index faces in crystal morphologies.
- The experimental verification performed for KBC crystal demonstrates their usefulness for the study of the growth phenomena and confirms our theoretical prediction that the fast-growing faces may enlarge their sizes and may be represented in final crystal morphology and that the slow-growing faces may decrease their sizes.

Appendix A

The correlation between growth rates of crystal faces and their sizes has been the object of experimental and theoretical studies for a long time. The correlation between the cross-section size l_{hkl} of a given hkl face, its growth rate, the growth rates of the neighbouring faces and appropriate interfacial angles is derived in Ref. [22]. The cross-section size l_{hkl} takes form [22]:

$$l_{hkl}=\frac{R_{h_1k_1l_1}\sin\gamma+R_{h_2k_2l_2}\sin\alpha-R_{hkl}\sin(\alpha+\gamma)}{\sin\alpha\sin\gamma}t+l^0_{hkl}, \tag{A1}$$

where R_{hkl}, $R_{h_1k_1l_1}$, $R_{h_2k_2l_2}$ are the normal growth rates of hkl, $h_1k_1l_1$, and $h_2k_2l_2$ faces, respectively, α and γ are the appropriate interfacial angles illustrated in Fig. 1, l^0_{hkl} — initial size of the hkl face (not marked in Fig. 1) and growth time t corresponds to the change of the size of the considered face from l^0_{hkl} to l_{hkl}. The initial size l^0_{hkl} may be considered as the size of a given face in the seed or after some time of growth (after growth of crystal layer). The constant growth rates R_{hkl}, $R_{h_1k_1l_1}$, $R_{h_2k_2l_2}$ are required not throughout the whole growth process but only during the growth of a layer of crystal that corresponds to the change of the size from l^0_{hkl} to l_{hkl}. After equating the numerator in Eq. (A1) to zero, it is possible to evaluate the so-called critical growth rate of the hkl face [23], which is denoted by $R^{\rm crit}_{hkl}$ and given by

$$R^{\rm crit}_{hkl}=\frac{R_{h_1k_1l_1}\sin\gamma+R_{h_2k_2l_2}\sin\alpha}{\sin(\alpha+\gamma)}. \tag{A2}$$

It is easier to explain the physical meaning of the idea of critical growth rate (Sec. 2) considering the ratio $R_{hkl}/R^{\rm crit}_{hkl}$, therefore Eq. (A2) should be inverted and multiplied by R_{hkl}. In this way we obtain Eq. (1).

On the other hand, in order to study the possibility of disappearance of the hkl face at its growth rate smaller than the growth rates of the neighbouring $h_1k_1l_1$ or $h_2k_2l_2$ faces, it is very convenient to consider the following quantities: $R^{\rm crit}_{hkl}/R_{h_1k_1l_1}$ and $R^{\rm crit}_{hkl}/R_{h_2k_2l_2}$.

First of all let us focus on the ratio $R^{\rm crit}_{hkl}/R_{h_1k_1l_1}$. Rearranging Eq. (A2) we obtain that

$$\frac{R^{\rm crit}_{hkl}}{R_{h_1k_1l_1}}=\frac{\sin\gamma+\frac{R_{h_2k_2l_2}}{R_{h_1k_1l_1}}\sin\alpha}{\sin(\alpha+\gamma)}. \tag{A3}$$

If the ratio $R^{\rm crit}_{hkl}/R_{h_1k_1l_1}$ takes values smaller than unity, this would mean that in the case when the hkl face grows with the growth rate R_{hkl} greater than $R^{\rm crit}_{hkl}$ it may decrease and, in consequence, it may disappear although it grows more slowly than the neighbouring $h_1k_1l_1$ face ($R_{hkl}/R_{h_1k_1l_1}<1$). The condition $R^{\rm crit}_{hkl}/R_{h_1k_1l_1}<1$ [13] is equivalent to

$$\frac{\sin\gamma+\frac{R_{h_2k_2l_2}}{R_{h_1k_1l_1}}\sin\alpha}{\sin(\alpha+\gamma)}<1. \tag{A4}$$

From the above inequality we may find relative growth rate $R_{h_1k_1l_1}/R_{h_2k_2l_2}$ for which the condition $R^{\rm crit}_{hkl}/R_{h_1k_1l_1}<1$ is satisfied. Such a condition is given by Eq. (2a) (Sec. 3.2).

In similar way, as in the case of $R^{\rm crit}_{hkl}/R_{h_1k_1l_1}$, we are able to consider the ratio $R^{\rm crit}_{hkl}/R_{h_2k_2l_2}$. Rearranging Eq. (A1) we obtain that [13]:

$$\frac{R^{\rm crit}_{hkl}}{R_{h_2k_2l_2}}=\frac{\frac{R_{h_1k_1l_1}}{R_{h_2k_2l_2}}\sin\gamma+\sin\alpha}{\sin(\alpha+\gamma)}. \tag{A5}$$

If $R_{hkl}^{\mathrm{crit}}/R_{h_2k_2l_2}$ may take values smaller than 1, this means that there is a possibility of disappearance of the hkl face at the growth rate smaller than the growth rate of the $h_2k_2l_2$ face — the other neighbouring face. The condition $R_{hkl}^{\mathrm{crit}}/R_{h_2k_2l_2} < 1$ is equivalent to the condition given by Eq. (2b) (Sec. 3.2).

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