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A study on the kinetic conditions corresponding to the growth of crystals of different morphologies

Jolanta Prywer

Institute of Physics, Technical University of Łódź, Wólczańska 219, 93-005 Łódź, Poland

E-mail: `jolantap@ck-sg.p.lodz.pl`

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Abstract. Crystals, even of the same substance, grown naturally or artificially take a variety of crystal morphologies which depend on growth conditions. This work contains the analysis of the kinetic conditions corresponding to the growth of crystals of different morphologies. The crystal chosen for exemplary calculations of kinetic conditions is wulfenite, which most often takes two different habits: platelet-like and elongated along the *c*-axis depending on growth conditions. In particular, kinetic conditions of the growth of both types of wulfenite crystal are given. Additionally, the kinetic conditions which correspond to gradual transformation from one habit into another are presented.

1. Introduction

Crystals grown naturally or artificially for industrial purposes most often do not exhibit the equilibrium forms, which satisfy the Gibbs law—the thermodynamic condition of the minimum surface free energy. The real crystal morphologies are determined by internal factors e.g. crystal structure or dislocations. The external factors such as supersaturation, temperature, pressure and presence of impurities also affect and control crystal habits. That is why the observed crystals, even of the same substance, take a variety of growth habits, different from those predicted theoretically [1, 2].

The aim of this paper is to present an analytical method with graphic representation for developing the kinetic conditions which correspond to the growth of crystals of different morphologies. The introduced method is illustrated by an example because it is impossible to develop kinetic conditions valid for all kinds of crystal, as the valid kinetic conditions must be found for every given crystal individually. As a crystal for which exemplary calculations are performed, the wulfenite crystal has been chosen. The reason for such a choice is that these crystals, during the growth process, take most often two extremely different shapes [3]: platelet-like or elongated along the *c*-axis. Such extreme shapes of growing crystals make it possible to easily illustrate the difference between habits and transient habits. In this paper the kinetic conditions corresponding to the growth of wulfenite crystals of these two habits and to the transformation from one growth shape into another are presented. Additionally, the manner in which one morphology changes into another is discussed. The wulfenite crystal has been chosen as an exemplary crystal, but such kinetic conditions may be derived for any crystal using the same principles.

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2. Kinetic conditions corresponding to the growth of crystals of different morphologies

2.1. Method of analysis

In order to explain different crystal habits, which appear during the growth processes, and to develop kinetic conditions corresponding to the growth of crystals of these habits, we use an idea of the critical growth rate R_A^{crit}. The critical growth rate R_A^{crit} is defined as the normal growth rate of the face A at which the given edge $l_{A/C}$ (shown in figure 1(a)), created by the faces A and C, preserves its size [4, 5]. It was derived in [4] and [5] that, in 3D crystals, the critical growth rate R_A^{crit} may be expressed by the formula:

$$R_A^{crit} = \frac{\sin\beta(R_B \sin\gamma \sin\psi_2 + R_D \sin\alpha \sin\psi_1) - R_C \sin\alpha \sin\gamma \sin(\psi_1 + \psi_2)}{\sin\beta(\cos\alpha \sin\gamma \sin\psi_2 + \cos\gamma \sin\alpha \sin\psi_1) - \cos\beta \sin\gamma \sin\alpha \sin(\psi_1 + \psi_2)} \quad (1)$$

where R_B, R_C and R_D are the normal growth rates of the individual faces B, C and D, respectively. The faces B, C and D are the surrounding faces of the edge $l_{A/C}$. The angles α, β, γ and ψ_1, ψ_2 are defined in figure 1(a). As it is mentioned above, generally, this critical growth rate R_A^{crit} means the growth rate of the face A at which the given edge $l_{A/C}$ preserves its size ($R_A/R_A^{crit} = 1$). If the initial size of this edge is equal to zero, zero size is preserved, which means that this edge does not appear in the habit. If the face A grows with the normal growth rate R_A greater than $R_A^{crit}(R_A/R_A^{crit} > 1)$, then the size of $l_{A/C}$ decreases or, if the edge does not exist in the habit it still does not appear. In the case when the growth rate R_A is smaller than $R_A^{crit}(R_A/R_A^{crit} < 1)$ the edge size increases, or if the edge does not exist in the habit it starts to appear and develops its size.

In order to investigate appearance, changes in size and disappearance of a whole face in a 3D crystal, it is sufficient sometimes to consider the changes in size of one edge of this face only, but sometimes it is not sufficient—it depends on the shape of a given face. There are faces of such shapes, e.g. some pentagonal faces, for which it is sufficient to consider the changes in size of one edge only [5]. This means that the disappearance of this edge is equivalent to the disappearance of the whole face. Then, we say that the edge represents a given face. However, there are faces of such shapes for which it is necessary to consider the changes in size of individual edges. In such cases the disappearance of one edge of a given face does not lead to the disappearance of the whole face [5]. The changes in size or disappearance of one edge may lead only to the changes in shape of the face and its size. Then, we say that one particular edge does not represent a given face.

The situation is different in a case of a cross-section of a crystal, which may be considered as a 2D crystal. Such a cross-section is shown in figure 1(b). Now, face A and the changes in its size are represented by an edge l_A. This edge is not a real edge of this face. It is a line connecting two opposite and parallel edges of this face. The changes in size of this edge correspond to changes in size of the whole face A and therefore, it is denoted by l_A, not $l_{A/C}$. Taking this into account and taking into account the fact that for 2D crystals $\psi_1 + \psi_2 = 180°$ [5], equation (1) reduces to the form [4, 5]:

$$R_A^{crit} = \frac{R_B \sin\gamma + R_D \sin\alpha}{\sin(\gamma + \alpha)}. \quad (2)$$

Similarly, as in the case of 3D crystals, the size of the face A, represented by the length of the edge l_A, depends on R_A/R_A^{crit} ratio. For $R_A/R_A^{crit} > 1$ the size of face A decreases, for $R_A/R_A^{crit} = 1$ the size is preserved and for $R_A/R_A^{crit} < 1$ the size increases.

The growth rates R_A, R_B, R_C and R_D require more detailed explanation. These growth rates are the growth rates of the faces A, B, C and D, respectively. In this paper, it is assumed that the growth rates of the individual faces are constant during the growth of single growth

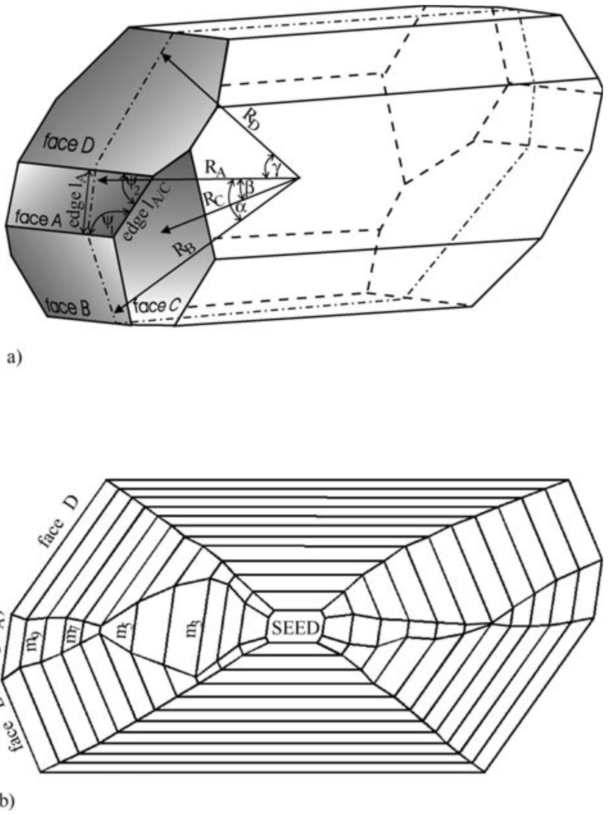

Figure 1. Hypothetical crystal drawn in order to illustrate: (a) an edge $l_{A/C}$, the faces A, B, C and D, surrounding this edge, and their normal growth rates R_A, R_B, R_C and R_D, respectively; α, β, γ—the interfacial angles; ψ_1, ψ_2—the complements of the angles between the directions defined by the appropriate edges of the face A. The dot and dash line indicates the position of the cross-section presented in (b). (b) The cross-section of this crystal which may be treated as a 2D crystal in which a given face A is represented by l_A. $m_3, \ldots, m_9$ denote the growth bands.

bands. Then, the distance between growth bands is proportional to the growth rates of the appropriate faces. For example, in figure 1(b), the distances between growth bands (from m_3 to m_6), visible on the face A growth sector, are growing bigger and bigger. This means that the consecutive growth bands of this face grow with bigger and bigger growth rates. The growth rate of this face is constant for a single growth band, but its value is different for each growth band. It may be also noticed, in figure 1(b), that the distances between growth bands of the neighbouring face B are the same for the whole growth process: this means that the growth rate of this face does not change during the growth process. From this it follows that the same growth band, but of some other face, grows with constant rate too, but these two constant growth rates do not have to be the same.

The investigations of internal morphologies, which are revealed in crystal cross-sections, are very advantageous. The internal morphology, in particular the growth bands, the growth sectors and their shapes make it possible to follow the behaviour of the habit during the growth process. Straight boundaries between adjacent growth sectors correspond to constant relative growth rates of the faces whose sectors created this boundary [1, 7]. There are also bent or zigzag boundaries between growth sectors [1, 7]. They indicate that the relative growth rates are not constant. For a given crystal, the relative growth rates may be simply measured as the distance between growth bands seen in the cleavage plane. Consequently, information about growth rates is obtained on the basis of analysis of sector zoning and growth banding.

On the other hand, it is possible to invert the above reasoning. Using analytical formulae (equations (1) or (2)) and substituting the values of faces growth rates and angles appropriate for any edge or face into these formulae it is possible to evaluate the critical growth rates R_A^{crit} for different edges or faces of a given crystal. As it is shown later in this paper, the critical growth rates R_A^{crit} are usually functions of appropriate relative growth rates of the neighbouring faces. However, sometimes the critical growth rate R_A^{crit} is constant and independent of the relative growth rates of the neighbouring faces. Having the critical growth rates R_A^{crit} which correspond to changes in sizes of different faces, we draw them in one graph in a Cartesian system (the graph of the critical relative growth rates). In the general case, the critical growth rates R_A^{crit} are planes 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, to different changes in habit. For example, one region may correspond to the appearance of a given face, another to the disappearance of some other face and still another to the existence of a face in the habit and development of its size. This means that, on the basis of such a graph, it is possible to develop kinetic conditions for growing crystals of different morphologies. Moreover, it is possible to draw, using computer simulation, 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 how the growth sectors, growth boundaries and, finally, the whole habit change in response to the changes of the relative growth rates of the individual faces.

The above is a short description of the introduced method. In order to make it more clear and understandable the presented method is applied to wulfenite crystal, which is chosen as an exemplary crystal.

3. Example of calculations of kinetic conditions for wulfenite crystals

In order to find out whether the proposed method of developing kinetic conditions of growth of crystals of different morphologies is acceptable, let us consider, as an example, a crystal grown in nature, namely wulfenite ($PbMoO_4$, point group 4, unit cell parameters: $a = b = 5.41$ Å, $c = 12.08$ Å [8]) which takes mostly two different crystal habits [3] depending on growth rates. The first one is a platelet-like habit; the second kind is a habit elongated along the c-axis (see figure 2). In regard to the number of faces, these two habits differ from each other by one set of faces only. In the elongated habits, the set of corner faces $\{1\bar{1}0\}$ appears, while in the platelet-like habits this set is absent. The fundamental difference between these habits is the size of some faces. Let us take a closer look at the face (001). In the platelet-like habits this face is quite big and its size is the same as the size of the opposite face $(00\bar{1})$ (not named in figure 2). In the elongated habit the face (001) is much smaller. The situation of the set {011} is contrary. It is seen that in platelet-like habits these faces are quite small in comparison with the size of these faces in the second kind of habit, the one elongated along the c-axis. The changes in size of both the face (001) and the set {011} influence the size of the set {012}. As a result, the faces from the set {012} become shorter (the length of these faces is smaller). However, the second dimension of these faces, let us call it the height of the faces, is almost unchanged. The remaining faces are of very similar sizes in both these two kinds of habit. Therefore, in order to investigate how it happens that the crystal habits that appear are so different, we should focus on the face (001) and the sets {012} and {011}, which demonstrate the biggest differences in sizes in both kinds of habit. The analysis of changes in size of these faces is reduced to the

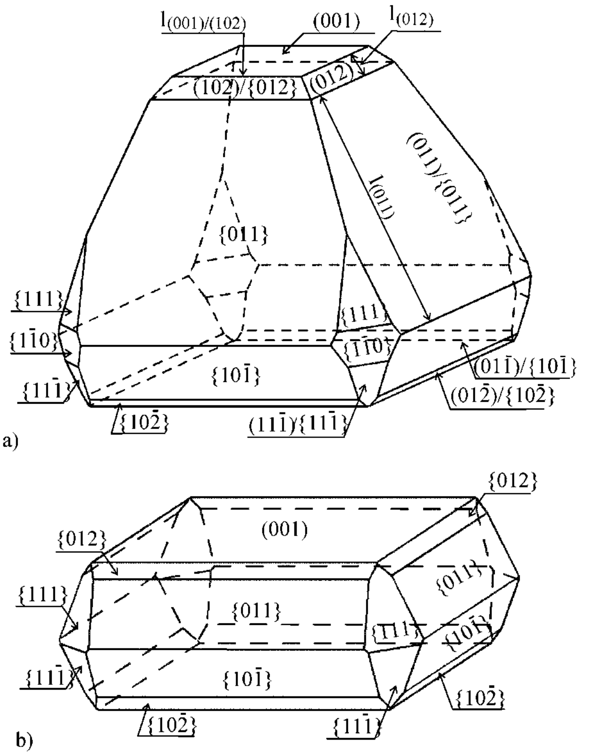

Figure 2. Two observed habits of a crystal grown in nature—wulfenite: (a) the elongated habit, (b) the platelet-like habit.

analysis of changes in lengths of appropriate edges of these faces. In all calculations presented below it is assumed that there is no anisotropy of growth rates of the faces belonging to all sets, with the exception of the set {001} described in subsection 3.1.

First, let us take a closer look at the set {012}, which demonstrates the smallest changes as compared to the face (001) and the set {011}. We focus on the changes in height of this set of the faces and we leave aside the changes in its length. In order to investigate the changes in height of these faces it is sufficient to investigate the changes in length of $l_{(012)}$ displayed in figure 2(a). As described in subsection 2.1, this is not strictly speaking an edge, it is only the line which connects two opposite and parallel edges of the face (012). The edge $l_{(012)}$ represents the whole face (012) and, as we do not consider the anisotropy of the growth rates of the faces belonging to a given set, $l_{(012)}$ also represents the whole set {012}. Therefore, we may consider the critical growth rate $R^{crit}_{\{012\}}$, not $R^{crit}_{(012)}$. In this case, in order to evaluate the critical growth rate $R^{crit}_{\{012\}}$, it is possible to apply equation (2) developed for 2D crystals. Substituting into equation (2) $R^{crit}_{(012)}$ as R^{crit}_{A}, $R_{(001)}$ as R_B, $R_{\{011\}}$ as R_D and taking the angles α and γ from table 1, row 1, we have that the critical relative growth rate $R^{crit}_{\{012\}}/R_{(001)}$ takes the following form:

$$\frac{R^{crit}_{\{012\}}}{R_{(001)}} = 0.33 + 0.82\frac{R_{\{011\}}}{R_{(001)}}. \tag{3}$$

It is seen that the $R^{crit}_{\{012\}}/R_{(001)}$ ratio is a linear function of the relative growth rate $R_{\{011\}}/R_{(001)}$, which may vary with growth conditions.

Table 1. The values of the angles α, β, γ between normals to the face pair and the values of the angles ψ_1, ψ_2 between the directions defined by corresponding edges for the wulfenite crystal. All these values of angles are computed by the program SHAPE and they are used in calculations concerning changes in size of given edge $l_{A/C}$ and as a result, of the whole face A.

Face A/set of faces	Edge $l_{A/C}$	Angle α = A/B	β = A/C	γ = A/D	ψ_1	ψ_2	Row
(012)/{012}	$l^{a}_{(012)}$	48.15°=(012)/(001)	—	17.73°=(012)/(011)	—	—	(1)
(001)/{001}	$l_{(001)/(102)}$	48.15°=(001)/(012)	48.15°=(001)/(102)	48.15°=(001)/(0$\bar{1}$2)	90.00°	90.00°	(2)
(011)/{011}	$l^{a}_{(011)}$	17.73°=(011)/(012)	—	48.25°=(011)/(01$\bar{1}$)	—	—	(3)

[a] this edge is considered as an edge l_A.

In order to precisely analyse the changes in size of the face (001) it is necessary to consider the changes in size of one of its edges, for example the edge $l_{(001)/(102)}$, which is surrounded by the faces belonging to the set {012}. The changes in size of this edge lead to changes in size of the whole face (001). Thus, we may evaluate the critical relative growth rate $R^{crit}_{(001)}/R_{\{012\}}$. The faces B, C, D are the faces belonging to the set {012}. Because here it is assumed that there is no anisotropy of growth rates in this set of faces, it may be written: $R_B = R_C = R_D = R_{\{102\}}$. Taking this into account and substituting into equation (1) the angles appropriate for the face (001) (table 1, row 2) and dividing by $R_{\{102\}}$ we obtain that the critical relative growth rate $R^{crit}_{(001)}/R_{\{012\}}$ is equal to:

$$\frac{R^{crit}_{(001)}}{R_{\{012\}}} = 1.50. \tag{4}$$

The ratio $R^{crit}_{(001)}/R_{\{012\}}$ is constant and independent of the growth rates of the neighbouring faces.

Finally, let us take a closer look at the set {011}. In order to investigate the changes in size of this set it is sufficient to investigate the changes in length of the edge $l_{(011)}$ (see in figure 2(a)), which represent the changes in size of the whole set {011}. Therefore, it is possible to apply equation (2) developed for 2D crystals. Substituting into this equation data given in table 1, row 3 and dividing by $R_{(001)}$, the critical relative growth rate $R^{crit}_{\{011\}}/R_{(001)}$ is equal to:

$$\frac{R^{crit}_{\{011\}}}{R_{(001)}} = 0.82\frac{R_{\{012\}}}{R_{(001)}} + 0.33\frac{R_{\{10\bar{1}\}}}{R_{(001)}}. \tag{5}$$

It is worth pointing out that the ratio $R^{crit}_{\{011\}}/R_{(001)}$ is a function of two variables: $R_{\{012\}}/R_{(001)}$ and $R_{\{10\bar{1}\}}/R_{(001)}$.

In this way we have found three dependences given by equations (3), (4) and (5), which deal with the size changes of the set {012}, the face (001) and the set {011}, respectively. The values of the critical relative growth rates estimated on the basis of these equations mean that for the relative growth rates $R_{\{012\}}/R_{(001)}$, $R_{(001)}/R_{\{012\}}$ and $R_{\{011\}}/R_{(001)}$ equal to the critical ones, the sizes of, respectively, the set {012}, the face (001) and the set {011} remain the same during the further growth process. The growth with the relative growth rates $R_{\{012\}}/R_{(001)}$, $R_{(001)}/R_{\{012\}}$ and $R_{\{011\}}/R_{(001)}$ smaller (greater) than critical leads to continuous increase (decrease) in the size of the set {012}, the face (001) and the set {011}, respectively.

In order to consider all these dependences in one graph, it is necessary to rearrange the equalities, aiming to have the same variables in all equations. It is very convenient to consider the dependence of $R_{\{012\}}/R_{(001)}$ on variables $R_{\{011\}}/R_{(001)}$ and $R_{\{10\bar{1}\}}/R_{(001)}$. To achieve this, we have to rearrange two equalities, namely equations (4) and (5), while equation (3) remains unchanged. In the case of equation (4) it is necessary to consider $R_{\{012\}}/R^{crit}_{(001)}$, and therefore we have:

$$\frac{R_{\{012\}}}{R^{crit}_{(001)}} = \frac{1}{1.50}. \tag{4a}$$

This means that for $R_{\{012\}}/R_{(001)} = R_{\{012\}}/R^{crit}_{(001)} = 1/1.50$ the initial size of the face (001) is preserved; for $R_{\{012\}}/R_{(001)}$ greater (smaller) than 1/1.50 the size of the face (001) increases (decreases). It is also necessary to rearrange equation (5) in order to have the required variables. Transforming equation (5) properly, we obtain:

$$\frac{R_{\{012\}}}{R_{(001)}} = \frac{R^{crit}_{\{011\}}/R_{(001)} - 0.33R_{\{10\bar{1}\}}/R_{(001)}}{0.82}. \tag{5a}$$

Now, it is possible to draw these three functions in one graph. Such a graph is shown in figure 3. Later on, this graph will be called the graph of the critical relative growth rates. Surface 1 in this figure illustrates the dependence given by equation (3), surface 2 that given by equation (4*a*) and surface 3 that given by equation (5*a*). Later on, surfaces 1, 2 and 3 will be called the surfaces of the critical relative growth rates $R^{crit}_{\{012\}}/R_{(001)}$, $R_{\{012\}}/R^{crit}_{(001)}$ and $R^{crit}_{\{011\}}/R_{(001)}$, respectively. These three crossing surfaces divide the space of the graph into seven regions: 'below', 'among 1, 2, 3', 'above', 'between 2 and 1, 3', 'between 3 and 1, 2', 'between 1, 2' and 'between 1, 3' as denoted in figure 3. The analysis of these regions is very important, especially in research of different crystal habits, the transition from one habit into another and the appearance of different faces. These practical applications are described below, in three subsections.

3.1. Different wulfenite crystal habits at constant growth rates for a given shape of seed

Each region of the graph presented in figure 3 corresponds to different changes in crystal habit because each of these regions corresponds to different relative growth rates. We may analyse the direct influence of the relative growth rates, from each region of the graph of the critical relative growth rates, on the habits of growing crystals. In order to make such an analysis easier we present in figure 4 the cross-sections of wulfenite crystals which correspond to each region of the graph. These cross-sections are obtained by computer simulation using the program SHAPE (version 4.1.1 professional [9]; the basic concepts of the software were published in 1980 [10]). Let us concentrate for a while on a shape of a seed from which the growth process proceeds. The seeds are seen in figure 4 at the bottom of each cross-section of the crystals. We assume in our discussion that the seeds possess all faces which appear in the final habits. The shape of the seeds and the sizes of the individual faces existing in the seeds for all cross-sections shown in figure 4 are the same. The seeds adhere to the basis by the face $(00\bar{1})$ (not named in figure 4). As the seeds grow crystals of different habits appear. As mentioned in section 3, we focus in this paper on the changes in size of the face (001) and two sets {012} and {011}, and we do not consider the changes in size of the sets $\{10\bar{1}\}$ and $\{10\bar{2}\}$. Therefore, we assume that the relative growth rate $R_{\{10\bar{1}\}}/R_{\{10\bar{2}\}}$ is constant and equal to 1.28 throughout the whole growth process for any region of the graph of the critical relative growth rates, and consequently for all cross-sections presented in figure 4. In contrast to this, the sets of faces {012}, {011} and the face (001) 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. Consistently, the cross-sections presented in figure 4 differ from each other in the relative growth rates $R_{\{012\}}/R_{(001)}$, $R_{\{011\}}/R_{(001)}$ and $R_{\{01\bar{1}\}}/R_{(001)}$. The theoretically assumed values of these relative growth rates for each cross-section are presented in table 2. Additionally, we

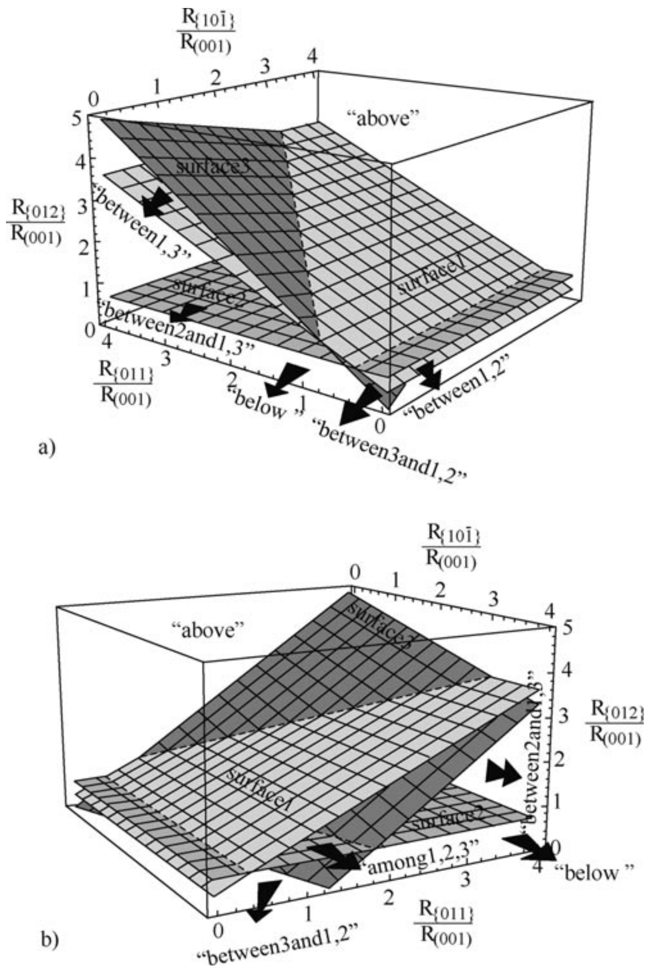

Figure 3. 3D graph of the critical relative growth rates: (a) and (b) two different views of the same graph. The surfaces 1, 2 and 3 are the surfaces of the critical relative growth rates $R^{crit}_{\{012\}}/R_{(001)}$, $R_{\{012\}}/R^{crit}_{(001)}$ and $R^{crit}_{\{011\}}/R_{(001)}$, respectively. The regions ‘below’, ‘among 1, 2, 3’, ‘above’, ‘between 2 and 1, 3’, ‘between 3 and 1, 2’, ‘between 1, 2’ and ‘between 1, 3’ created by these crossing surfaces 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.

are assuming that the growth rate of the face $(00\bar{1})$, which adheres to the basis, is equal to zero. The growth rate of the opposite face (001) may take various values (but constant for a given cross-section). The set {001} is an exception, because generally it is assumed that there is no anisotropy of growth rates of the faces belonging to a given set. This assumption is made for simplicity, but in real crystals the growth rates of the faces belonging to the same set may differ slightly. In such cases the tetragonal symmetry of these crystals is disordered.

The cross-sections, presented in figure 4, allow us to analyse and follow the changes in the habit of wulfenite crystals, which occur in response to changes in the relative growth rates, corresponding to each region of the graph of the critical relative growth rates. First, we consider the region called ‘below’. This region lies below all three surfaces of appropriate critical relative growth rates. This means that for the relative growth rates from this region,

Table 2. The theoretically assumed relative growth rates $R_{\{012\}}/R_{(001)}$, $R_{\{011\}}/R_{(001)}$ and $R_{\{10\bar{1}\}}/R_{(001)}$ corresponding to wulfenite crystal cross-sections shown in figure 4. The relative growth rate $R_{\{10\bar{1}\}}/R_{\{10\bar{2}\}}$ is assumed to be constant for all cross-sections and equal to 1.28.

	$R_{\{012\}}/R_{(001)}$	$R_{\{011\}}/R_{(001)}$	$R_{\{10\bar{1}\}}/R_{(001)}$
Figure 4(a)—'below'	0.60	0.64	0.42
Figure 4(b)—'among 1, 2, 3'	1.32	1.26	0.87
Figure 4(c)—'above'	1.07	0.89	0.63
Figure 4(d)—'between 2 and 1, 3'	0.96	1.03	0.62
Figure 4(e)—'between 3 and 1, 2'	0.63	0.49	0.39
Figure 4(f)—'between 1, 2'	0.63	0.36	0.28
Figure 4(g)—'between 1, 3'	2.85	3.03	1.79

the face (001) and the set {011} decrease their sizes while the size of the set {012} increases. This is shown in figure 4(a). Here, during the growth, the initial sizes of the face (001) and of the set {011} decrease, while the initial size of the set {012} increases. Both the sets $\{10\bar{1}\}$ and $\{10\bar{2}\}$ increase their sizes, which ensues from the assumed value of the relative growth rate $R_{\{01\bar{1}\}}/R_{\{10\bar{2}\}}$ equal to 1.28. It is seen that the crystal development with the growth rates from this region unavoidably leads to the development of crystals of habits elongated along the c-axis.

Let us take a closer look at the region called 'among 1, 2, 3' (figure 3(b)). This region lies among three surfaces of the critical relative growth rates. Strictly speaking, this region is above surfaces 2, 3 and below surface 1. From this, it follows that for the relative growth rates from this region the face (001) and both the sets {012} and {011} increase their sizes. Such a situation is shown in figure 4(b). It is seen that all these faces increase their initial sizes and, for the assumed values of appropriate relative growth rates (see table 2), the crystal morphology developed is platelet-like, very similar to that observed in nature.

Now, let us focus on the region called 'above' (figure 3). This region is above all the three surfaces of the critical relative growth rates. The development with the growth rates from this region guarantees the increase in the sizes of the face (001) and the set {011} and, simultaneously, the decrease of the size of the set {012}. Such a situation is shown in figure 4(c). It may be noticed that this habit, drawn for the assumed values of the relative growth rates (see table 2), is a little similar to that observed in nature. The faces of the set {011} are very well developed, while the faces of the set {012} are not. However, it is not exactly platelet-like or elongated crystal. We may call this shape a transient habit.

In a similar way, we may analyse the other regions of the graph of the critical relative growth rates presented in figure 3. In order to make such an analysis easier, the changes in sizes of all considered faces (001), {012} and {011} which correspond to all regions of the graph are shown in table 3 and, additionally, the cross-sections of habits, which correspond to these regions, are shown in figures 4(d)–(g). It may be noticed that some of them are transient (see figure 4(d)), some elongated (see figures 4(e), (f)), and some of them are platelet-like (see figure 4(g)).

The above analysis reveals that, depending on appropriate relative growth rates, the morphology of wulfenite crystals changes from platelet-like to elongated along the c-axis, and additionally transient habits may occur, although such habits have never been reported. Based on the graph of the critical relative growth rates, displayed in figure 3, and on figure 4, which illustrates appropriate cross-sections corresponding to each region of this graph, we may conclude that the relative growth rate $R_{\{012\}}/R_{(001)}$ in relation to $R_{\{012\}}/R^{crit}_{(001)}$ has the deciding influence on the morphology of the growing wulfenite crystals. If $R_{\{012\}}/R_{(001)}$ is smaller than

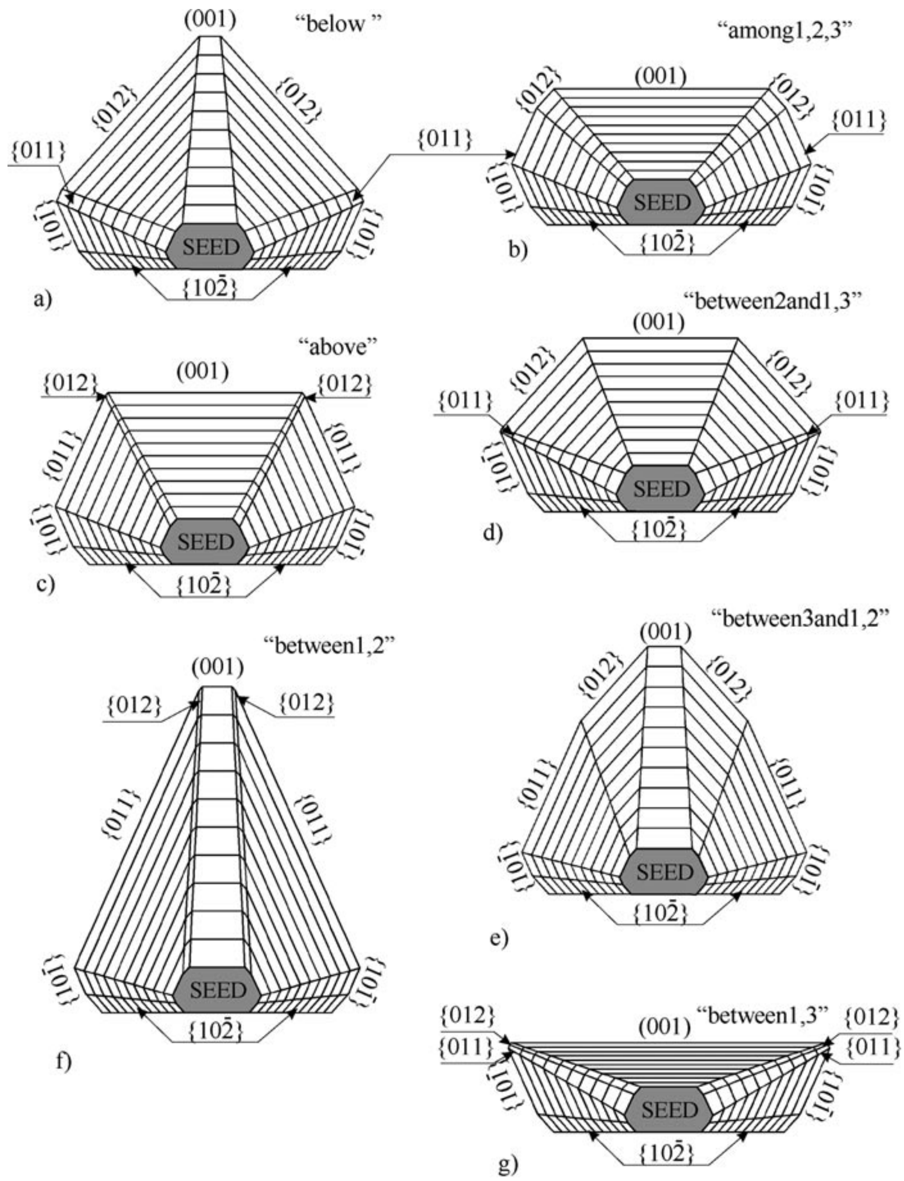

Figure 4. The exemplary cross-sections of wulfenite crystal habits which correspond to different regions of the graph of the critical relative growth rates presented in figure 3. For all these cross-sections the growth begins from identical seeds. The number of growth bands and the time distance between growth bands is the same.

$R_{\{012\}}/R_{(001)}^{crit} = 1/1.50$ (below surface 2), the face (001) has a tendency to decrease, which leads to the growth of the elongated crystals. This applies to all regions below surface 2: for 'below' see figure 4(a), 'between 3 and 1, 2' see figure 4(e) and 'between 1, 2' see figure 4(f). If $R_{\{012\}}/R_{(001)}$ is exactly equal to the critical $R_{\{012\}}/R_{(001)}^{crit} = 1/1.50$ (the ratio $R_{\{012\}}/R_{(001)}$ is on surface 2) the initial size of the face (001) does not change, which, for the considered shape of seed, also corresponds to the growth of crystals of the elongated habits.

Table 3. The changes in sizes of the individual faces which correspond to appropriate regions of the graph presented in figure 3. Symbol ↑ means that a given face appears in the habit or, if it exists in the habit, it increases its size in a given region of the graph; symbol ↓ means that a given face does not appear in the habit or, if it exists, it decreases its size in a given region of the graph.

	{012}	(001)	{011}
'below'	↑	↓	↓
'among 1, 2, 3'	↑	↑	↑
'above'	↓	↑	↑
'between 2 and 1, 3'	↑	↑	↓
'between 3 and 1, 2'	↑	↓	↑
'between 1, 2'	↓	↓	↑
'between 1, 3'	↓	↑	↓

The situation is different above surface 2, i.e. for $R_{\{012\}}/R_{(001)}$ greater than 1/1.50. It refers to the regions: 'between 1, 3', 'between 2 and 1, 3', 'among 1, 2, 3' and 'above'. Depending on the value of $R_{\{012\}}/R_{(001)}$ in relation to $R_{\{012\}}/R^{crit}_{(001)}$ the crystal may develop elongated, transient or platelet habit, in all these regions of the graph. Generally, the bigger the value of the relative growth rate $R_{\{012\}}/R_{(001)}$, the more platelet-like is the crystal morphology (cf table 2). We may follow this analysis by looking at figure 4. Here, we can see four habits for which the relative growth rate $R_{\{012\}}/R_{(001)}$ is above surface 2 (greater than 1/1.50). Those habits are, respectively, shown in figures 4(b), (c), (d), (g). Taking into account the value, from the highest to the lowest, of the relative growth rate $R_{\{012\}}/R_{(001)}$, the sequence of these habits is as follows: the habit in figures 4(g), 4(b), 4(c) and the last is the habit in figure 4(d). It may be noticed that two crystals shown in figure 4(b) and 4(g) have explicit platelet-like habits. Two other habits are transient habits between platelet-like and elongated. We have shown earlier that the elongated crystals grow for the relative growth rate $R_{\{012\}}/R_{(001)}$ equal to and smaller than 1/1.50. However, let us take a closer look at figure 5, which illustrates an elongated habit. The crystal of such a habit grows for the relative growth rates $R_{\{012\}}/R_{(001)}$, $R_{\{011\}}/R_{(001)}$ and $R_{\{01\bar{1}\}}/R_{(001)}$ equal to 0.71, 0.49 and 0.39, respectively, which corresponds to the region 'among 1, 2, 3'. It should be noticed that the relative growth rate $R_{\{012\}}/R_{(001)}$, equal to 0.71, is only a little greater than the critical ($R_{\{012\}}/R^{crit}_{(001)} = 1/1.50$). The growth with the relative growth rate $R_{\{012\}}/R_{(001)}$ greater than the critical $R_{\{012\}}/R^{crit}_{(001)}$, but very close to the critical value, leads to continuous and slow increase in size of the face (001), which corresponds, in consequence, to the growth of the elongated crystals. Therefore, we may conclude that the elongated crystals grow for the relative growth rate $R_{\{012\}}/R_{(001)}$ not only smaller than critical $R_{\{012\}}/R^{crit}_{(001)}$, but also for a little greater than critical (very close to surface 2); we assume that this happens up to $R_{\{012\}}/R_{(001)} = 0.80$.

On the basis of the above considerations, we conclude that the elongated crystals grow for all regions, but only up to the relative growth rate $R_{\{012\}}/R_{(001)} = 0.80$. It should be emphasized that for the regions: 'below', 'between 3 and 1, 2' and 'between 1, 2' the crystals take only elongated habits, because they are below surface 2 (with $R_{\{012\}}/R_{(001)}$ smaller than the critical $R_{\{012\}}/R^{crit}_{(001)}$). The transient habit of crystals is predicted in the following regions: 'between 1, 3', 'between 2 and 1, 3', 'among 1, 2, 3' and 'above' but for $R_{\{012\}}/R_{(001)}$ within the range $(0.80, 1.20\rangle$. Crystals of platelet-like habits grow for the same regions as transient ones but for $R_{\{012\}}/R_{(001)}$ greater than 1.20.

It is worth noticing that these kinetic conditions, for growing wulfenite crystals of different morphologies, are obtained for a given shape of a seed and for constant growth rates of faces.

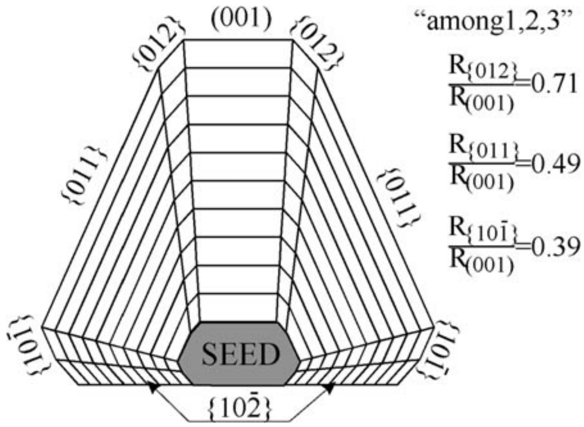

Figure 5. The exemplary cross-section of the wulfenite elongated habit which corresponds to appropriate relative growth rates (region 'among 1, 2, 3').

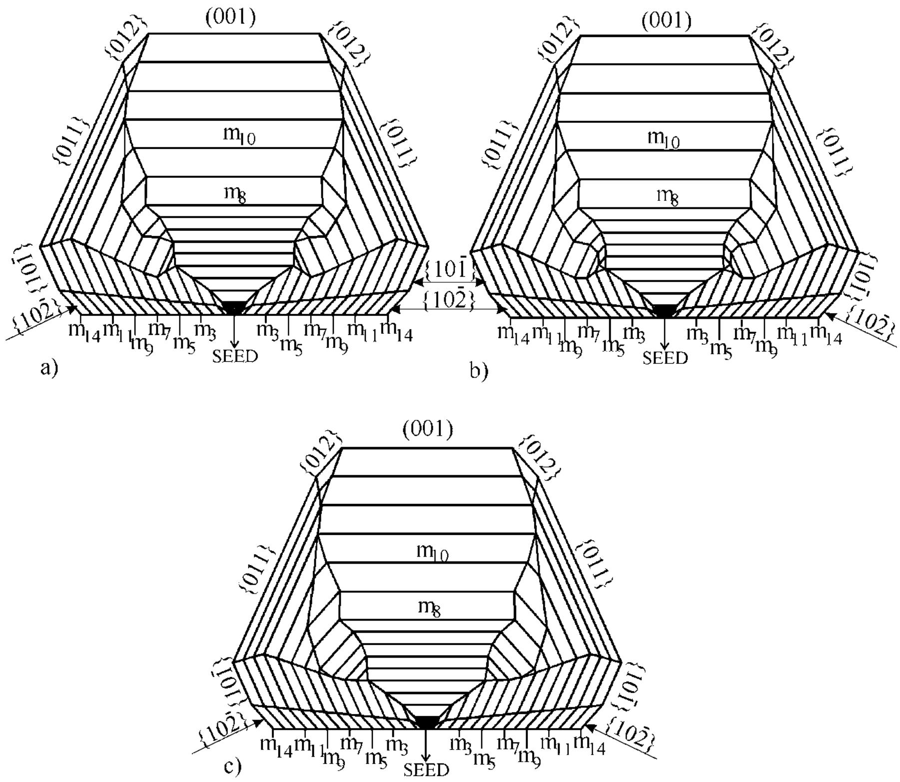

Figure 6. Three cross-sections through wulfenite crystals illustrating different ways of growth of crystals of the same external habits: (a) at first, the set {011} appears, then the set {012} appears; (b) simultaneous appearance of both these sets {011} and {012}; (c) at first the set {012} appears, then the set {011} appears. m_3 to m_{14} denote the growth bands.

For another morphology of the seed the physical sense of each region of the graph of the critical relative growth rates should be considered with special attention. For example, in the considered case of a seed possessing all faces which appear in the final habit, the region 'between 2 and 1, 3' corresponds to an increase in size of the face (001). For a seed without this face, this region would correspond to the appearance of this face.

The obtained results show that for constant growth rates and for a considered shape of seed the relative growth rate $R_{\{012\}}/R_{(001)}$ in relation to $R_{\{012\}}/R^{crit}_{(001)}$ has the deciding influence on the final morphology of wulfenite crystals. Then, the following question arises. For what purpose do we consider the relative growth rates $R_{\{011\}}/R_{(001)}$ and $R_{\{10\bar{1}\}}/R_{(001)}$? These two relative growth rates also influence the crystal habit, especially the relative growth rate $R_{\{011\}}/R_{(001)}$, but in a lower degree than $R_{\{012\}}/R_{(001)}$. Therefore, we do not analyse this in detail. It should be remembered that our calculations serve as an example to illustrate the practical applications of the introduced method for developing kinetic conditions. We may predict only, but without going into details, that the relative growth rates $R_{\{011\}}/R_{(001)}$ and $R_{\{10\bar{1}\}}/R_{(001)}$ influence the proportion in which the appropriate faces appear in the final habit. For example, for the cross-section shown in figure 4(b) the relative growth rates $R_{\{10\bar{1}\}}/R_{(001)}$ and $R_{\{011\}}/R_{(001)}$ are equal to 0.87 and 1.26 (table 2), respectively, which corresponds to the proportion of the size of the sets {011}, {012} and the face (001), which is very similar to that observed in the platelet-like crystal grown in nature (cf figure 2(b)). This means that the faces of the set {012} are quite small while the faces of the set {011} are well developed.

It should be emphasized that the cross-sections of wulfenite crystals presented in figure 4 are obtained for constant relative growth rates of appropriate faces. This means that these relative growth rates, for a given cross-section, lie in the same region of the graph. A question arises. Is the 'transition' of the relative growth rates from one region to another, for example from 'above' to 'among 1, 2, 3' possible? The observations of cross-sections of real crystals reveal, beside straight boundaries, which correspond to constant relative growth rates, bent or zigzag boundaries between growth sectors. They indicate that the relative growth rates are not constant. Therefore, the answer for the above question is: yes, it is possible, but not for constant relative growth rates. How such a possibility influences the crystal habit we will consider in the next subsection.

3.2. The transition from platelet-like habit to that elongated along the c-axis at varying growth rates

Let us consider the history of growth of one wulfenite crystal, chosen as an example, and shown in figure 6(a). The majority of boundaries between growth sectors is not straight but they take a more or less zigzag shape. This means that the growth rates are not constant during the whole growth process. They take a constant value only for a single growth band of the growing crystal but each growth band may grow with different growth rate—cf comments on growth rates in subsection 2.1. The only straight boundary is between growth sectors of the faces belonging to the sets $\{10\bar{1}\}$ and $\{10\bar{2}\}$. This ensues from the fact that we do not analyse in the present paper the changes in size of these faces and we have assumed, as in subsection 3.1, that the relative growth rate $R_{\{10\bar{1}\}}/R_{\{10\bar{2}\}}$ is constant and equal to 1.28. It is seen that the growth begins from a very small seed. This seed, in contrast to that considered in subsection 3.1, does not possess all faces which appear in the final habit. This seed adheres to the basis by the face $(00\bar{1})$ and the growth rate of this face is assumed to be equal to zero. The seed possesses also the opposite face (001) and two sets $\{10\bar{1}\}$ and $\{10\bar{2}\}$. The changes in the relative growth rates of the other faces, which may take different values, lead to the changes in habit of the growing wulfenite crystal. We may easily analyse and clearly explain the behaviour of this growing crystal presented in figure 6(a), knowing the physical sense of each region of the graph of the critical relative growth rates presented in figure 3.

Beginning from the seed up to the m_3 growth band, the seed increases its size (see figure 6(a)); in particular the face (001) increases, which corresponds to the relative growth rate $R_{\{012\}}/R_{(001)}$ lying above surface 2. Up to the m_3 growth band, the sets of faces {011} and {012} are absent. This means that the relative growth rates $R_{\{012\}}/R_{(001)}$ and $R_{\{011\}}/R_{(001)}$ are greater than the critical. As a result, for this stage of growth, the relative growth rates lie in the region 'between 1, 3'. We say concisely and conventionally that the crystal is in the region 'between 1, 3'. Beginning from the m_3 growth band, the faces of the set {011} begin to appear. We may suspect that the rapid changes of growth conditions or the change of growth mechanism cause the rapid 'transition' of the relative $R_{\{011\}}/R_{(001)}$ growth rate from the region 'between 1, 3' to the region 'above'. This leads to the appearance of the set {011}. The situation changes again beginning from the m_5 growth band. At this growth band the next set {012} appears. The crystal is in the region 'among 1, 2, 3' and remains in this region up to the m_6 growth band. Between m_6 and m_7 growth bands, the crystal is in the region 'between 2 and 1, 3' because the faces of the set {012} increase while the faces of the set {011} decrease their size. The situation is inverted between m_7 and m_8 growth bands. Here, the faces belonging to the set {011} increase, while the faces belonging to the set {012} decrease. Therefore, the crystal is in the region 'above'. Up to this stage of growth, the crystal is in a thin platelet-like shape. In other words, if the crystal stopped growing at this stage of growth it would be in a platelet-like shape. However, the growth process continues and, beginning from the m_8 growth band, the crystal morphology starts to transform into another shape.

Between the m_8 and m_9 growth bands, the face (001) does not change in size and, simultaneously, both the sets {011} and {012} increase their sizes. This corresponds to the region 'among 1, 2, 3'. However, it should be noticed that the face (001) does not change its size, which means that the relative growth rate $R_{\{012\}}/R_{(001)}$ is exactly equal to the critical $R_{\{012\}}/R^{crit}_{(001)}$ value. The crystal 'lies' on surface 2, but within the region 'among 1, 2, 3'. During the further part of growth, from the m_9 to m_{11} growth band the face (001) and the set {011} increase their sizes, while the set {012} decreases in size and, as a result, it disappears at the m_{11} growth band. At this stage of growth the crystal is in the region 'above'. Although the face (001) still increases its size, the crystal is not strictly in a thin platelet-like shape. From the m_9 to m_{11} growth band the crystal morphology is in a transient shape.

During the further growth, until the end of growth, the size of the face (001) fluctuates a little, but with a tendency to decrease. The relative growth rates are such that the crystal tends to be in an elongated shape. At m_{12} growth band the faces of the set {012} reappear and the faces of the set {011} still have a tendency to increase. From this, it follows that the crystal is in the region 'between 1, 2' from the m_{11} to m_{12} growth band and in the region 'between 3 and 1, 2' from the m_{12} to m_{14} growth band. Both these regions are below surface 2. As a result of this growth the crystal morphology transforms into a habit elongated along the *c*-axis.

In this subsection we proved that for varying relative growth rates the 'transition' of the relative growth rates from one region of the graph of the critical relative growth rates to another is possible. Such a 'transition' leads to the changes in habit of the growing crystal. On the basis of the analysis performed for wulfenite crystals we may suspect that the transition from one habit into another is possible also in the case of other crystals. With a graph of critical relative growth rates for another crystal it is possible to establish at which values of the relative growth rates such a transition may occur.

3.3. The analysis of faces appearing, not appearing and disappearing from crystal habit

The growth of crystals of very similar or even the same external morphologies may run in different way. For example, figure 6 illustrates three different histories of growth of wulfenite crystals, of which the external habits are very similar—the final sizes of the individual faces for all these three crystals are almost the same, but the way of growth is different. The main difference is the sequence of appearance of the sets {011} and {012}. In figure 6(a) at first, at the m_3 growth band, the set {011} appears and later, at m_5 growth band, the set {012} appears. In the case of the crystal shown in figure 6(b) both these two sets appear simultaneously at the m_3 growth band. For the crystal shown in figure 6(c) at first, at the m_3 growth band, the set {012} appears and then, at the m_6 growth band, the set {011} appears.

The appearance of the set {012} is possible for the relative growth rates lying below surface 1. The appearance of the set {011} is possible for the relative growth rates lying above surface 3. The common regions lying below surface 1 and simultaneously above surface 3 are regions 'among 1, 2, 3' and 'between 3 and 1, 2'. Only for the relative growth rates from these regions may the considered sets {012} and {011} appear simultaneously. The only difference between these regions deals with the face (001). In the region 'among 1, 2, 3' the face (001) increases while in the region 'between 3 and 1, 2' the face decreases. This means that for the cross-section shown in figure 6(b) the relative growth rates are in the region 'among 1, 2, 3' at the m_3 growth band.

For the cross-section shown in figure 6(a), at the m_3 growth band the crystal is in the region 'above' which corresponds to the appearance of the set {011} and during the further growth, at the m_5 growth band the set {012} appears. This means that the relative growth rates 'transit' into the region 'among 1, 2, 3'. The situation is different in the case of the cross-section shown in figure 6(c). Here, at the m_3 growth band the set {012} appears which corresponds to the region 'between 2 and 1, 3'. Later, at the m_6 growth band, the set {011} appears, which corresponds to the 'transition' of the relative growth rates to the region 'above'.

From the analysis presented in this subsection it follows that the introduced method, based on the graph of the critical relative growth rates, gives the possibility to research the conditions of appearance of different faces. This method is also useful for developing kinetic conditions corresponding to a given face not appearing in the crystal habit. For example, we can imagine for a while that sometimes the wulfenite crystals grow without the set of faces {012}. This means that the crystal would never grow with the relative growth rates lying in all regions below surface 1.

4. Conclusions

Our current work is considering the possibility of developing kinetic conditions corresponding to the growth of crystals of different morphologies. It is shown that, based on the analytical formulae (1) and (2), we may evaluate critical relative growth rates, which correspond to changes in length of crystal edges or changes in size of whole faces of a given crystal. For some edges or faces, the critical relative growth rates are functions of the relative growth rates of the neighbouring faces; for other edges or faces they take constant value independent of the relative growth rate of the neighbouring faces. By drawing these functions, in the general case, in one 3D graph we create a graph of the critical relative growth rates. In such a graph each critical relative growth rate is represented by a surface in a space of the graph. Sometimes these surfaces cross each other, sometimes not—they are parallel. Anyway, these surfaces divide the space of the graph into appropriate regions of the relative growth rates, which correspond to different morphologies of growing crystals. In other words, such a graph is a starting-point to develop kinetic conditions which correspond to different morphologies of any crystal. It should be pointed out that this method, based on such a graph, gives the possibility of developing kinetic conditions for constant growth rates as well as for varying growth rates and, additionally, for different shapes of seed. Besides, the developed method has another useful property—it allows us to analyse the kinetic conditions which correspond to the appearance, or not, and disappearance of faces in crystal habit.

Keeping in mind that it is impossible to derive one and the same kinetic conditions valid for all crystals, the wulfenite crystal is chosen as an exemplary crystal for which the kinetic conditions corresponding to the growth of different morphologies are developed. This crystal growing in nature takes mostly two different habits: platelet-like and elongated along the c-axis. On the basis of the graph of the critical relative growth rates, made for this crystal, it is established that the deciding influence on the shape of these crystals has the relative growth rate $R_{\{012\}}/R_{(001)}$ in relation to the critical relative growth rate $R_{\{012\}}/R^{crit}_{(001)}$. Depending on the value of this relative growth rate the wulfenite crystals are elongated along the c-axis ($R_{\{012\}}/R_{(001)} < 0.80$), platelet-like ($R_{\{012\}}/R_{(001)} > 1.20$) or they are in a transient shape (for $R_{\{012\}}/R_{(001)}$ within the range $\langle 0.80, 1.20\rangle$).

The method presented in this paper for developing kinetic conditions corresponding to the growth of crystals of different morphologies, may be applied to any crystal. This method would be more valuable if growth rates of individual faces were connected with growth conditions, for example with temperature and supersaturation. Although researchers are still making attempts to do that, it is still a challenge for the future. However, the obtained results show that the use of the developed method is predictive and guide us to conduct investigations more accurately.

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