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On the Prediction of Crystal Morphology. II. Symmetry Roughening of Pairs of Connected Nets

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In commemoration of J. D. H. Donnay (1902–1994)

Abstract

Within the framework of the periodic bond chain analysis for the prediction of crystal morphology, connected nets play a crucial role. For a face (*hkl*) often more than one connected net is found. Symmetry relations between such connected nets can give rise to symmetry roughening of nets. In this paper, all cases where symmetry may lead to symmetry roughening are derived. The role of a mother phase in contact with the crystal is explicitly taken into account. It turns out that cases of symmetry roughening are, in a sense, complementary to situations where the classical Bravais–Friedel–Donnay–Harker selection rules apply.

1. Introduction

In paper I of this series, a physical basis was given for the classical Hartman–Perdok or periodic bond chain (PBC) analysis which is used to predict the morphology of a crystal from the crystal structure in terms of bonds between growth units (Grimbergen, Meekes *et al.*, 1998). So far, the bond energies have only played a minor role in the treatment. They will, however, be dealt with in a following paper. In paper I, mainly the determination of F faces, *i.e.* those (flat) faces that may occur on an equilibrium or growth form of a crystal in terms of connected nets, has been treated. An F face (*hkl*) was defined as a crystal face (*hkl*) with a roughening temperature higher than 0 K. The derivation and analysis of all connected nets of a crystal face offer a convenient way to determine whether a face is an F face or not. Statistical thermodynamic models of surfaces of relatively simple crystal structures play a key role in this analysis. As explained in paper I, a connected net (*hkl*) is a graph made up of points (representing the growth units) connected by bonds formed by the combination of at least two intersecting non-parallel so-called direct chains. A connected net (*hkl*) is repeated over a distance d_{hkl}, which is the interplanar distance of faces (*hkl*). The effect of a mother phase on the stability of an F face was explicitly taken into account. References to survey papers on PBC analysis can be found in paper I.

A kind of roughening, namely symmetry roughening, which is typical for certain pairs of equivalent connected nets was also introduced. One often finds pairs of connected nets for a face (*hkl*) that are mutually equivalent according to the space-group symmetry. Some of these pairs turn out to give rise to symmetry roughening of the corresponding crystal face at $T = 0$ K. In this paper, symmetry roughening is investigated in more detail. Another more practical reason for studying the effect of symmetry relations between connected nets of a crystal face is the large amount of connected nets that may be found for a single face. To avoid a superfluous energy calculation for such pairs, rules based on symmetry arguments and the physics of the roughening transition are derived in order to predict such a roughening in advance. This will be even more important for F faces that merely have such pairs of connected nets as such a face will not show up on a crystal form despite the presence of connected nets.

All cases where symmetry may lead to symmetry roughening are derived. A distinction is made between pairs of connected nets giving rise to microscopic symmetry roughening, leading to a macroscopically flat face, and pairs giving rise to macroscopic symmetry roughening for which the face gets rough even macroscopically. Analogously to paper I, the role of a mother

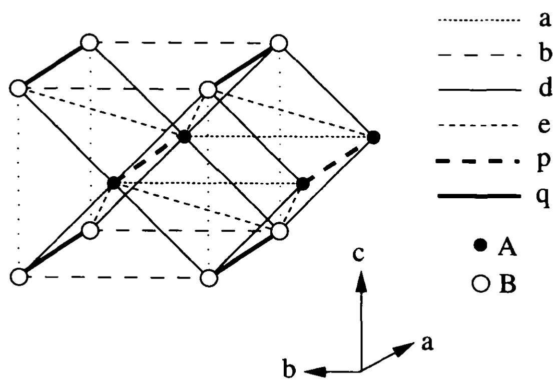

Fig. 1. Model crystal graph. The space group is $P1$; bonds d actually consist of bonds d_1 to d_4 in the (100) face (not indicated); bonds e also consist of four different bonds.

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phase in contact with the crystal is explicitly taken into account.

This paper is organized as follows. First, the phenomenon of symmetry roughening will be explained and illustrated for one specific example. In the next section, all symmetry elements that may lead to symmetry roughening will be derived and studied when the effect of a mother phase is neglected for some examples of connected nets. Such cases are referred to as a broken-bond description (Grimbergen, Meekes *et al.*, 1998). The effect of the presence of a mother phase will then be treated. The generalization to any crystal graph completes the classification. In the *Discussion*, the findings are summarized and put in a broader perspective. Finally, *Conclusions* are given.

2. Symmetry roughening

An example is given of an F face having a pair of connected nets that gives rise to symmetry roughening. Consider the crystal graph presented in Fig. 1. The unit cell contains one growth unit A and one growth unit B. This graph differs from the model graph used in paper I. The stoichiometry is still AB, though the symmetry is drastically reduced as a starting point for each example treated and it is, thus, assumed that the symmetry of the corresponding crystal is $P1$. Labelling of bonds and growth units is also different compared with paper I. Furthermore, bonds e are added. As a consequence of the absence of symmetry, the bonds d actually consist of four different bonds d_1 to d_4 in the (100) face of the unit cell. Also, bonds e consist of four different bonds. In Fig. 1, we do not make this distinction for the sake of clarity. In the examples that follow, sometimes some of the bonds are neglected although always a connected crystal graph is considered. Mainly the [100] and [001] projections of the graph for different symmetry elements, which are added temporarily, resulting in triclinic or monoclinic space groups, are studied. As a result, frequently space groups are mentioned that do not conform to the standard settings. This is a result of the choice to treat all cases within the same crystal graph for the sake of clarity. In all cases, the space-group symbols explicitly give the setting and, thus, the orientation of a mirror or rotation axis. It has to be noted that when drawing (crystal) graphs only the topology is relevant and actual crystallographic angles may differ from 90° depending on the space-group symmetry of the crystal considered. An important distinction has to be made between symmetry elements with and without a non-primitive translation. Homogeneous symmetry elements such as a mirror, an n-fold rotation axis and the inversion have no non-primitive translation and are elements of point groups. The term inhomogeneous symmetry element is used for glide planes and screw axes having a non-primitive translation. Later, the symmetry of the crystal in general is discussed.

As an example of symmetry roughening consider the case that there is a horizontal mirror plane m_z through the layers of growth units A (and B). As a result, the four different bonds d_1 to d_4 now are equivalent in two pairs denoted d_1 and d_2, respectively. For the moment, the bonds a, b and e are neglected. The mirror symmetry is destroyed for a semi-infinite crystal in contact with a mother phase as was discussed in paper I. For the moment, however, the effect of a mother phase is neglected, implying also that any surface reconstruction is ruled out, analogously to paper I.

Fig. 2 shows that for the orientation (001) two connected nets can be identified which are related by the horizontal mirror plane. Bonds p and q make the nets of the figure connected in two dimensions. In the figure also, a cut that starts along the connected net $(001)_1$, makes a step to the connected net $(001)_2$ and follows the latter one is indicated. Such a profile corresponds to the same broken-bond energy per surface mesh area as a pure $(001)_1$ or $(001)_2$ connected net. In other words, the step energy of the artificial step is zero. Although there are two connected nets present, the face (001) always gets rough as the step energy equals zero. The (001) face can have many such steps, both from $(001)_1$ to $(001)_2$ and from $(001)_2$ to $(001)_1$ without any difference in broken-bond energy. Such a face is rough as long as there is no other connected net possible for that orientation. In the example, this is the case as $(001)_1$ and $(001)_2$ are the only connected nets possible according to the definition.

This example of roughening related to the presence of a symmetry element was already mentioned by Bennema & van der Eerden (1987). The example in Fig. 2 shows a case where the connected nets of the symmetry pair are situated at different heights along the face normal. This results in a roughening in the sense that on a macroscopic scale the face rounds off. It is also possible that the connected nets are at the same height, for example, owing to a mirror perpendicular to the face. In such a case, the pair gets rough in the sense that no distinction can be made between the two connected nets. The face, then, stays flat on a macroscopic scale. The

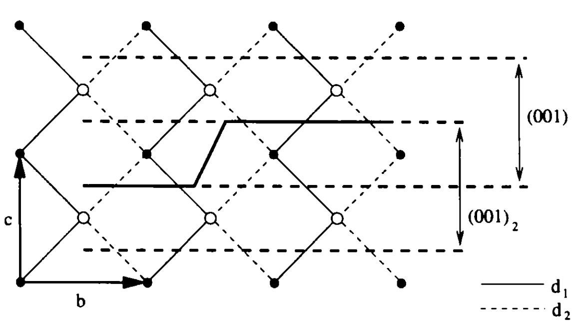

Fig. 2. Symmetry roughening for the (001) connected nets. The [100] projection is drawn. A homogeneous horizontal mirror plane m runs through the growth units. The solid line follows a path from $(001)_1$ to $(001)_2$ without cost of energy.

distinction between these two kinds of symmetry roughening is discussed below in more detail.

3. Possible cases of symmetry roughening

3.1. *Relevant symmetry*

The relevant symmetry is the space-group symmetry of the crystal; this is the complete symmetry for an infinite crystal. There are two important restrictions that lower the symmetry.

(i) The symmetry of a semi-infinite crystal, that is, a crystal on one side bounded by a (flat) face, is generally lower. As will be seen, only the local symmetry of the connected nets is relevant for symmetry roughening. Nevertheless, surface reconstruction can affect this local symmetry severely. The presence of a mother phase can put even more restrictions on the symmetry considerations. This symmetry reduction has been treated in paper I. For the moment, it is assumed that, if a mother phase is present, its effect, as far as symmetry is concerned, is negligible and also surface reconstruction is neglected.

(ii) In order to find the connected nets, the crystal is reduced to the crystal graph, which is defined by points made up of the growth units of the crystal, together with the bonds. Generally, the points are at the centre of mass of those growth units. Therefore, for a connected net (and also for the crystal graph), the symmetry is generally higher than for the corresponding connected net (crystal), defined on the positions of all atoms or ions of the crystal. As a result, we, sometimes, will have to reconsider the actual space-group symmetry of the crystal.

In general, the space group G is the group $\{R_i \| g_i\}$, where R_i are all elements of the point group K. The translations g_i consist of primitive translations of the lattice Λ together with the relevant non-primitive translations. The non-primitive translations depend on the choice of the origin. The primitive translations are only needed for the symmetry group of the unit cell and depend also on the growth unit or bond under consideration. Using this convention allows one to restrict oneself to the R_i together with the non-primitive translations modulo the primitive translations when considering the symmetry restrictions on the connected net. One has to bear in mind, however, that the primitive translations of R_i, in the case of a connected net, are those that bring the growth units and bonds back into the connected net. In other words, the unit cell of the connected net as determined by the interplanar distance $\mathbf{d}_{hkl}$ and a mesh area $\mathbf{M}_{hkl}$ is considered. The mesh area is defined by $\mathbf{d}_{hkl} \cdot \mathbf{M}_{hkl} = V$, where V is the volume of the unit cell of the crystal. To be more precise, the symmetry G_s of the *slice* corresponding to the connected net will be the relevant one. The subscript s is dropped in the following. A connected net is denoted by $\mathbf{k}^n_{hkl}$, where the superscript n labels the different connected nets possible for the F face (hkl) having a normal $\mathbf{k}_{hkl}$, where $|\mathbf{k}_{hkl}| = 1/d_{hkl}$. If not leading to confusion, the indices hkl or the label n are suppressed.

In general, $R \in G$ transforms a connected net $\mathbf{k}$ into another connected net $\mathbf{k}'$. Note that growth units at the end position $\mathbf{c}^e_j \in \mathbf{k}$ of a bond j are equivalent (symmetry related) to those at $\mathbf{c}^{e'}_j \in \mathbf{k}'$ and that this also holds for starting positions of the bond at $\mathbf{c}^s_j$ and $\mathbf{c}^{s'}_j$. Therefore, also the bonds $\mathbf{b}_j \in \mathbf{k}$ and $\mathbf{b}'_j$ are equivalent. Thus, the bond energies of $\mathbf{b}_j$ and $\mathbf{b}'_j$ are equal and even the connected net energy $E^{\text{slice}} = \sum_j E(\mathbf{b}_j)$ is the same for $\mathbf{k}$ and $\mathbf{k}'$.

3.2. *Orientation*

A general transformation $R \in K$ transforms a connected net $\mathbf{k}$ into another connected net $\mathbf{k}'$ with a different orientation. Note that a different orientation is also found if $\mathbf{k}' = -\mathbf{k}$. The latter case has been called a case of boundary swapping in paper I.

For a different orientation, the symmetry element R only implies that if the net $\mathbf{k}$ leads to a stable F face $\mathbf{k}$, the face $\mathbf{k}' = R\mathbf{k}$ is as stable.

For example, a fourfold rotation axis parallel to the c axis ensures that the faces (and all of its connected nets) (100), $(\bar{1}00)$, (010) and $(0\bar{1}0)$ are equivalent and have the same slice energy E^{slice}.

Symmetry elements that change the orientation of the connected net such that $\mathbf{k}' \neq \pm\mathbf{k}$ cannot give rise to symetry roughening. One can, and it is usually more efficient, apply the symmetry elements that transform a connected net into one with a different orientation in advance, thus decreasing the number of nets that have to be checked on connectedness or for which the energy has to be calculated.

3.3. *Orientation-conserving symmetries* ($\mathbf{k}' = \mathbf{k}$)

One can, in the case that $\mathbf{k}' = \mathbf{k}$, limit the discussion to symmetry elements that conserve the orientation of a connected net. The special case of boundary swapping, that is $\mathbf{k}' = -\mathbf{k}$, will be treated below. Therefore, a certain connected net $\mathbf{k}$ is considered. The symmetry elements R that leave its orientation invariant are (glide) mirror planes and (two-, three-, four- and sixfold) rotation (screw) axes that are perpendicular to the net and thus parallel to $\mathbf{k}$.

For these symmetry operations, one can distinguish four different situations.

3.3.1. *Singlet due to a homogeneous symmetry element.* Consider the case that the symmetry operation R is a homogeneous mirror plane or a homogeneous two-, three-, four- or sixfold axis perpendicular to the connected net. If the connected net is transformed into itself, it is called a singlet and there is no symmetry roughening.

3.3.2. *Doublet due to a homogeneous symmetry element.* The second situation considered refers to the case that the net, owing to a homogeneous symmetry operation, is not transformed into itself. Then, the symmetry element gives rise to equivalent connected nets that are at the same height with respect to $\mathbf{d}_\mathbf{k}$. A doublet, triplet, quadruplet or sextet of equivalent connected nets is found for, respectively, a two-, three-, four- or sixfold rotation axis. A mirror plane gives rise to a doublet. All multiplets can be reduced to sets of doublets. In these cases it is, sometimes, possible to make a path *via* bonds from one connected net to the other without energy cost. The consequences of this will be worked out in §3.3.4.

3.3.3. *Doublet due to an inhomogeneous symmetry element; BFDH.* The case of a screw axis or a glide plane perpendicular to the connected net **k** always imposes restrictions.

In the case of the repeated action of an n-fold screw axis, one obtains n mutually equivalent connected nets with thickness $d_\mathbf{k}/n$ that differ in height as seen along the screw axis. When the mutual shift between the connected nets is an integer times $\mathbf{d}_\mathbf{k}$, the situation reduces to the case of §3.3.1; otherwise, the n mutually equivalent connected nets $\mathbf{k}^n_{hkl}$ lead to a 'selection rule' for the face $\mathbf{k}_{hkl}$. For example, an n-fold screw axis parallel to the c axis leads to the selection rule that $(00l)$ can only be an F face if $l = nm$ $(m \in Z)$.

Analogously, the case of a glide plane perpendicular to the connected net **k** with the glide direction not perpendicular to **k** is considered. Now, one finds two equivalent connected nets that are mutually translated along the glide direction, which imposes restrictions on the Miller indices corresponding to the glide direction. For example, a glide plane a perpendicular to the b axis gives rise to the selection rule that $(h0l)$ can only be an F face if $h = 2m$ $(m \in Z)$.

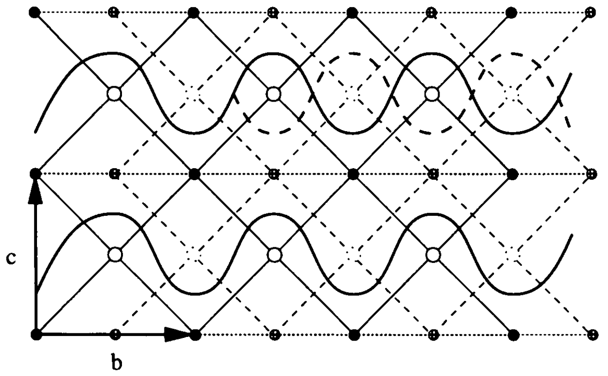

Fig. 3. Symmetry roughening for a pair of (001) connected nets owing to a glide plane perpendicular to the face for which the glide is perpendicular to **k**. The [100] projection is drawn. The mirror plane is in the plane of the figure and the dashed net is translated over $[0\frac{1}{2}0]$ with respect to the solid net; the space group is $Pb11$. Bonds b and e are neglected. The symmetry roughening is microscopic.

These restrictions are already well established and are covered by the Bravais–Friedel–Donnay–Harker (BFDH) law (Friedel, 1911; Donnay & Harker, 1937; Hartman, 1973, 1978).

In particular, the laws derived by Donnay & Harker impose these restrictions on the possible F faces. The (connected) nets that are restricted by such selection rules consist in the case of an n-fold screw axis of n (possibly connected) nets with thickness $d_\mathbf{k}/n$ and with mutually the same structure. For a glide plane, two equivalent connected nets are obtained that are translated over the non-primitive glide translation. In other words, the connected nets restricted by the BFDH law need not be checked on connectedness anyway. In such a case, one has to test the nets with smaller thickness according to the selection rules. Bravais and Friedel treated the selection rules due the choice of a non-primitive cell. These are rather straightforward as such a choice has direct impact on the indices (hkl).

In conclusion, in the case of a glide plane (with a component of the glide along **k**) or a screw axis, all faces perpendicular to these are restricted by the selection rules, which are the same as the limiting reflection conditions used in diffraction. As the BFDH rules have been formulated for complete slices, only the general conditions are relevant. The BFDH rules are relevant only for cases where boundary swapping plays no role, that is, they apply always, even in the presence of a mother phase.

In the modern formalism where the emphasis is laid on the connected nets, the special conditions also play a role. The latter only apply if all growth units of the connected net are at the corresponding special positions. In that case, one has to be careful and make a distinction between the actual molecule and the centre of gravity. If special conditions apply for a connected net for the inhomogeneous symmetry elements discussed in this section, the BFDH rules already restrict the analysis to one of the two connected nets. For other orientations (hkl) not restricted by the BFDH rules, however, one can have pairs of connected nets. All such cases are covered by the other sections of this paper. In other words, the special conditions are automatically taken into account as the symmetry group of the slice corresponding to the connected net is considered.

The connected nets that obey the BFDH law still might lead to symmetry roughening due to other symmetry elements.

3.3.4. *Doublet due to an inhomogeneous symmetry element; non-BFDH.* For the connected nets that fulfil the conditions imposed by the BFDH law, one can still find pairs of connected nets for which the nets are mutually equivalent *via* one of the orientation-conserving symmetry operations. As the symmetry elements relevant for the BFDH selection rules can give no further restrictions on the nets obeying these rules, one is left with the case of a glide plane perpendicular to the connected net with the glide perpendicular to **k**. This symmetry element can give rise to symmetry roughening. Note that the connected nets of such a pair are at the same height with respect to $d_{\mathbf{k}}$. The situation is somewhat comparable to that of §3.3.2. An example can be found in Fig. 3. In this figure, the [100] projection of the model graph of Fig. 1 is again drawn. Bonds *b* and *e* are neglected and bonds *p* and/or *q* run along the projection direction. A *b*-glide plane perpendicular to the *a* axis is added and the space group becomes *Pb*11. As a result, the number of atoms in the unit cell is doubled, which is indicated by the dashed net in Fig. 3. The bonds *d* still consist of four different bonds each being doubled by the mirror. Horizontal bonds between the growth units *A* are maintained in order to have the whole crystal graph connected. The solid wavy lines represent a slice of one of the connected (001) nets of a pair. The second one is partly drawn with a dashed wavy line. A transition over a distance d_{001} results in a nonzero step energy, ensuring a finite Ising transition temperature for the individual connected nets (Grimbergen, Meekes *et al.*, 1998). This pair of connected nets gets rough because a transition between the two nets can be made without energy cost as the same bonds are broken per mesh area. Therefore, the roughening does not result in a rounding off of the face; the two connected nets are at the same height. Fig. 3 alternatively represents the situation for space group *P*1*a*1.

The simplest example as far as the crystal is concerned, however, is that of a glide plane that transforms growth unit *A* into *B*. Consider, for instance, the (100) connected net in the [001] projection of Fig. 1 as presented in Fig. 4. In this example, bonds *a*, *b* and *d* are neglected. As this graph is rather complicated, the [010] projection showing the zigzag pattern of the bonds *e* for the two connected nets is also drawn. The relevant space groups are *P*1*c*1 and *P*11*b*. Bonds *p* and/or *q*, which are now symmetry related, make the nets connected. The four different bonds *e* are due to the glide plane grouped into two sets of bonds denoted e_1 and e_2. In this case, we, again, are dealing with two connected nets, as indicated in the figure, which are at the same height. Again, a transition between the two nets can be realised with no energy cost.

As mentioned before, the situation dealt with in §3.3.2 is comparable with that of this section. In fact, Figs. 3 and 4 besides some minor details also illustrate the situations of space group *P*1*m*1 or *P*112 and of space group *P*211, respectively. To understand this, note that in the basic crystal graph of Fig. 1 the position of growth units *A* is arbitrary as the space group for this figure is *P*1.

In conclusion, one finds that for orientation conserving symmetry elements ($\mathbf{k}' = \mathbf{k}$) the BFDH selection rules are complementary to the situations where symmetry roughening can take place. Symmetry roughening is limited to the cases of a glide plane perpendicular to the connected net with the glide perpendicular to **k** and to the case of a homogeneous plane or a homogeneous two-, three-, four- or sixfold axis perpendicular to the connected net giving rise to doublets. In all these cases, the two connected nets which are symmetry related are at the same height. Obviously, no symmetry roughening is found for singlets.

3.4. *Orientation-inverting symmetries* ($\mathbf{k}' = -\mathbf{k}$)

A new case arises when one considers the symmetry elements that invert the orientation of a connected net. These are a mirror or a twofold axis parallel to the connected net and the inversion. In this case, the upper and lower sides of the connected net are interchanged and one can speak of boundary swapping. Now, one can again distinguish four situations. The different cases are again distinguished by the presence of a non-primitive translation but now also by the position of the symmetry element along the face normal. There exist special positions of a connected net for a symmetry element if the net is transformed into itself modulo primitive translations. Such singlets are non-polar, that is, despite the boundary swapping, the mother phase interacts in the same way with the two surfaces (Grimbergen, Meekes *et al.*, 1998). If the symmetry element is not at a special position of the connected net, the transformed net will be displaced along the face normal and the corresponding members of the doublet will differ in height and/or lateral position. A polar connected net cannot be a singlet under orientation-inverting symme-

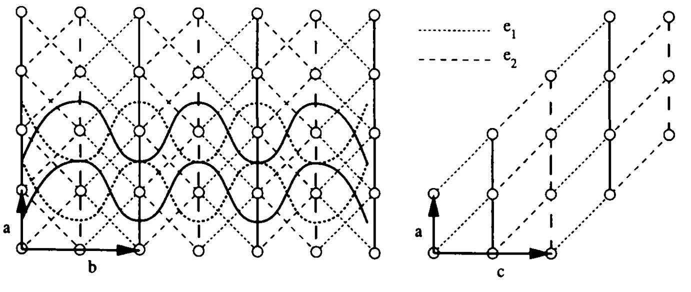

Fig. 4. Symmetry roughening for a pair of (100) connected nets owing to a glide plane perpendicular to the face for which the glide is perpendicular to **k**. The space group is *P*1*c*1 or *P*11*b*. Both the [001] projection (left) and the [010] projection (right) are drawn. The vertical bonds are *p* and *q* bonds; they are symmetry related in this case but still indicate the rows of former growth units *A* and *B*, respectively.

tries. Note that the special positions of a connected net, in general, differ from those of the unit cell.

3.4.1. *Singlet due to a symmetry operation at a special position.* For a twofold (screw) axis or a (glide) mirror plane parallel to the connected net or the inversion, the symmetry operation transforms the net into itself modulo a primitive translation if the symmetry operation is at a special position of the connected net. We, then, are dealing with a singlet again. Despite that, formally, one can speak of boundary swapping and effectively there is no difference in the surface structure. In such a case, the (single) net is non-polar and there is no restriction.

3.4.2. *Doublet due to a homogeneous symmetry operation.* For a homogeneous symmetry element giving rise to boundary swapping, symmetry roughening can occur, namely when the element is not at a special position of the connected net. The net can be polar or non-polar. In such a case, the two connected nets of the pair have a height difference. An example can be found in Fig. 5. The graph in this figure represents again the [100] projection of the graph of Fig. 1. Bonds *e* are neglected. It illustrates a situation for which the space group is *P*11*m*, *P*211 or *P*121. Therefore, the space group $P\bar{1}$ is also covered by this example. The unit-cell content is doubled. Still, the bonds *d* consist of four different bonds, each doubled by the symmetry operation. A horizontal bond between the growth units is added in order to have the whole crystal graph connected. The graph suggests a smaller unit cell owing to the symmetry imposed. This is a case where the symmetry of the graph is higher than that of the crystal. The centres of gravity represent for example a polar molecule with a dipole moment parallel to **k**. The wavy solid line represents a slice of one of the connected nets of a pair. The second net symmetry related to the first one is represented by the dashed wavy cut. As the figure shows, again, a transition between the two nets can be made without energy cost. Hence, the pair gives rise to macroscopic symmetry roughening when broken bonds are considered.

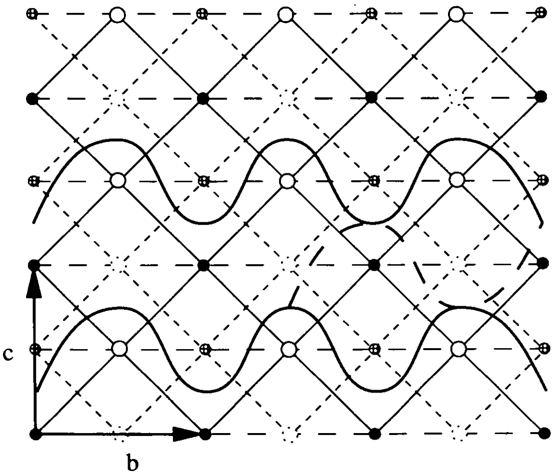

Fig. 5. Symmetry roughening for a pair of (001) connected nets. The space group is *P*11*m*, *P*211 or *P*121. The [100] projection is drawn. The dashed cut is the symmetry image of the solid cut.

Note that, as in the case of Fig. 2, the two connected nets of the pair would give rise to roughening because the transition from the solid to the dashed net in Fig. 5 can be continued to the solid net one interplanar distance higher, again without energy cost.

3.4.3. *Doublet due to an inhomogeneous symmetry operation not at a special position.* Next, the case of an inhomogeneous symmetry element not on a special position of the connected net is considered. Firstly, the case that the symmetry operation gives rise to two equivalent connected nets translated along a non-primitive translation parallel to the net is treated. There is no height difference for the doublet. In fact, Fig. 3 can be interpreted also to serve as an example for this case. For this, the space group is assumed to be *P*11*b* or $P12_11$. However, in contrast to the situation dealt with in §3.3.4, in this case there is boundary swapping. Note that the symmetry element acts on the growth units and not on the boundary of the cuts.

There is no difference in broken-bond energies and even a path from one of the nets to the other does not cost any energy. Therefore, the pair still gives rise to microscopic symmetry roughening.

Secondly, the situation of a glide plane or twofold screw axis perpendicular to **k** but not at a special position of the connected net, giving rise to two nets also differing in height along the face normal, will be treated. Fig. 5 can serve as an illustration for space groups $P2_111$ or *P*11*a*. Also in this case, a transition between the two nets can be made without cost of energy. Hence, the pair gives rise to macroscopic symmetry roughening in a broken-bond treatment.

4. The presence of a mother phase

The situations described above change when one considers a crystal in contact with a mother phase. Then, the description in terms of broken bonds, in principle, no longer holds. As discussed in paper I, only a few symmetry elements of the crystal survive in the situation of a semi-infinite crystal in contact with a mother phase in the absence of reconstruction and assuming that at least topologically the outer layers of the surface are comparable to the bulk structure. These symmetry elements are the rotation axes perpendicular to the face and a mirror or glide plane perpendicular to the face with the glide along the face. This severe symmetry reduction occurs because successive layers in the crystal near the surface will interact differently with the mother phase. Of course, the interaction can be extremely complicated owing to adsorbed complexes, reconstruction *etc.* For the problem of symmetry roughening, however, it is assumed that only the symmetry properties of the outermost layer determining the degeneracies in energy are relevant. Topologically, this layer will be comparable with a corresponding bulk layer when no reconstruction is present. Therefore, energies may differ but the symmetry properties remain intact up to the polarity of a layer. In other words, it is assumed that, when a step is realised on a surface, the vanishing of the step free energy owing to symmetry is determined by the symmetry of the bulk crystal. Nevertheless, for polar cuts, there will be a difference in surface energy owing to the mother phase in the case of boundary swapping.

As an example, the first case of Fig. 2 is reconsidered. The two alternative connected nets $(001)_1$ and $(001)_2$ will interact differently with the mother phase. Therefore, the mirror symmetry will be lost for, at least, the outermost layer, be it $(001)_1$ or $(001)_2$. Hence, the surface energies for the two will be different. Thus, the symmetry roughening caused by this pair vanishes when a mother phase is present.

If the symmetry element giving rise to boundary swapping is at a special position of the connected net, the two boundaries will be equivalent. In such a case, the interaction with the mother phase will be the same for the two boundaries and the pair still gives rise to symmetry roughening.

5. More complicated crystal graphs

The question arises whether the classification in terms of symmetry presented in the previous sections also holds for more complicated connected nets. In order to study this, one can simply add bonds to the nets studied up to now. As an example, reconsider the case of Fig. 5. If one adds an arbitrary bond to the graph, the symmetry operation generates equivalent bonds. In Fig. 6, the situation is drawn. Any such equivalent bond is again cut as many times by the solid wavy boundary as it is by the dashed wavy boundary. There is one type of bond, however, that can destroy symmetry roughening. If one reconsiders the case of Fig. 3, one can again add any bond and its symmetry-equivalent ones. In this case, however, there is one kind of bond that is not cut as often on making a transition from one of the two equivalent connected nets to the other. Such a bond is a horizontal bond cut by the boundary. The situation is illustrated in Fig. 7. As a result, such a transition in the presence of a horizontal bond that is cut by the two connected nets always favours a repeated jump from one connected net of the pair to the other.

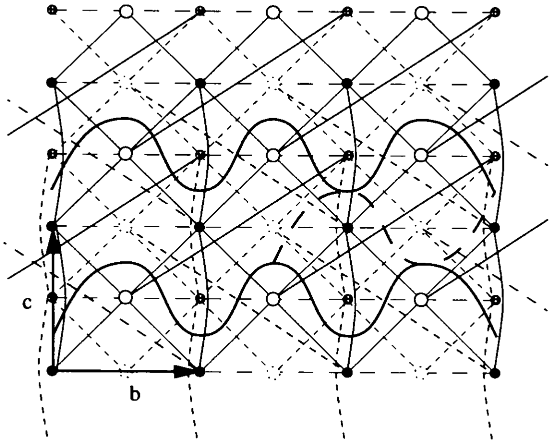

Fig. 6. Symmetry roughening for the pair of (001) connected nets of Fig. 5. Two new bonds have been added. The dashed bonds are the symmetry image of the solid ones.

It is easily verified that for a situation for which symmetry roughening occurs for a pair of connected nets with no height difference combined with a horizontal bond cut by the boundaries there exists an alternative connected net owing to a repeated jump between the nets.

Although the alternative net can be less stable than each of the pairs of connected nets, as the horizontal bond energy can be (very) small compared with the difference between the lower d bonds and the upper ones in Fig. 7, in such a case, the symmetry roughening of the pair is lifted. In conclusion, one finds that the minimum demand for the phenomenon of symmetry roughening is the existence of a doublet. If any bond perpendicular to **k** would destroy the symmetry roughening, there exists an alternative surviving connected net.

6. Discussion

The results obtained up to now are summarized in Table 1. Symmetry roughening covers different kinds of roughening for which the step (free) energy is zero already at $T = 0$ K. The major difference between symmetry roughening and well known kinds of rough-

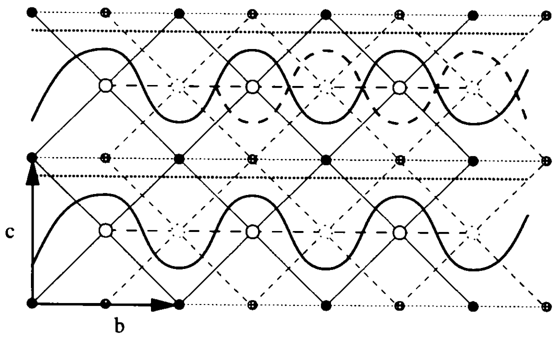

Fig. 7. Symmetry roughening for the pair of (001) connected nets of Fig. 3. The added horizontal bond between the growth units B, cut by the wavy boundary, is omitted once on a transition from the solid to the wavy boundary. An alternative flat connected net in this situation is indicated.

Table 1. *Cases of symmetry roughening for a crystal in the broken-bond description and for a crystal in contact with a mother phase*

$\mathbf{k}' = R\mathbf{k}$; m: (glide) mirror plane; 2, 3, 4, 6: (screw) axes; BFDH: Bravais–Friedel–Donnay–Harker rules apply; SR: symmetry roughening; sh: doublet consisting of nets at the same height; dh: doublet consisting of nets at different heights; sp: special position for the connected net; np: non-polar net.

	R		Vacuum	Mother phase
$\mathbf{k}' \neq \pm\mathbf{k}$			No restrictions	No restrictions
$\mathbf{k}' = \mathbf{k}$	$m \parallel \mathbf{k}$	Homogeneous	Singlet or SR; sh	Singlet or SR; sh
		Glide $\perp \mathbf{k}$	SR; sh	SR; sh
		Glide not $\perp \mathbf{k}$	BFDH	BFDH
	2, 3, 4, 6 $\parallel \mathbf{k}$	Homogeneous	Singlet or SR; sh	Singlet or SR; sh
		Screw	BFDH	BFDH
$\mathbf{k}' = -\mathbf{k}$	$m \perp \mathbf{k}$	Homogeneous or glide at sp, np	Singlet	Singlet
		Homogeneous not at sp	SR; dh	No restrictions
		Glide not at sp	SR; sh or dh	No restrictions
	$2 \perp \mathbf{k}$	Homogeneous or screw at sp, np	Singlet	Singlet
		Homogeneous not at sp	SR; dh	No restrictions
		Screw not at sp	SR; sh or dh	No restrictions
	$\bar{1}$	At sp, np	Singlet	Singlet
		Not at sp	SR; sh or dh	No restrictions

ening such as thermal roughening and kinetical roughening is that the latter kinds of roughening take place for temperatures $T > 0$ K. Symmetry roughening can occur in the case of doublets of connected nets. In that light, only connected nets that are singlets and have a thickness d_{hkl} according to BFDH give rise to F faces.

This definition is appropriate when referred to crystal graphs because there the relevant bonds are already chosen. When referred to the actual crystal, one has to realise that at low temperatures more and more weak bonds become relevant for the stability of the crystal and its faces. Such additional bonds strictly speaking could destroy the symmetry roughening at lower temperatures.

In a sense, symmetry roughening is an artifact as a result of the pursuit of F faces in terms of connected nets and the definition of an F face as a crystal face (hkl) with a roughening temperature larger than zero. The exhaustive determination of all F faces for any crystal in terms of that definition, however, is at the moment only feasible *via* a determination of all connected nets, as discussed in paper I. An analysis of all connected nets simply implies the rejection of appropriate pairs for which symmetry roughening occurs.

A kind of symmetry roughening can also occur in a situation for which the symmetry between the relevant bonds has an accidental nature.

Note that while symmetry roughening imposes restrictions on the F faces as they are rough at 0 K, the BFDH rules impose restrictions on the choice of faces (and thus connected nets) because of the existence of a thinner slice with the same surface energy. As the symmetry elements relevant for BFDH never cause boundary swapping, the corresponding rules always hold, even in the presence of a mother phase.

Coming back to symmetry roughening, an important distinction has to be made between cases for which the pair consists of connected nets at the same height and ones for which they differ in height with respect to the direction of **k**.

If the nets only have a zero step (free) energy for transitions between nets at the same height, the corresponding face does not get rough macroscopically. The only result is that it is impossible to make a distinction between the nets on a microscopic scale. In such a case, the steps can be considered as domain walls between surface domains having a configuration corresponding to the two connected nets. The free energy corresponding to a step with height d_{hkl} is still finite. Therefore, these nets lead to a stable F face. Microscopic roughening is related to the situation of so-called disordered flat (DOF) phases found in statistical thermodynamical solid-on-solid models with next-nearest-neighbour interactions (Rommelse & den Nijs, 1987; den Nijs & Rommelse, 1989). Such a situation can lead to increased growth rates (Grimbergen, Meekes *et al.*,, 1998; Grimbergen, Bennema & Meekes, 1998).

For symmetry roughening of a pair of connected nets at different height, the face gets rough macroscopically if there is no alternative singlet connected net present. Looking at Table 1, one finds that the only cases where macroscopic symmetry roughening can take place are those for which boundary swapping occurs due to symmetry elements not at special positions of the connected net. The same table shows that such a macroscopic symmetry roughening is, in principle, lifted in the case of a mother phase in contact with the crystal face. In any case, macroscopic symmetry roughening will not appear when the orientation (hkl) has a singlet because the latter ensures that the roughening temperature for the orientation will be larger than 0 K. Microscopic symmetry roughening can still occur even if a singlet is present.

In general, the symmetry of a crystal can be higher than that of the monoclinic and triclinic cases treated up to now. In order to test the presence of symmetry roughening for any face (*hkl*), one can select all symmetry elements of the space group that leave $\mathbf{k}_{hkl}$ invariant up to a sign and use Table 1 as a reference. One symmetry element giving rise to symmetry roughening is enough to discard the pair of connected nets if no alternative singlet is present. One has to bear in mind, however, that only symmetry roughening with a height difference gives rise to a macroscopic roughening effect and that the presence of a mother phase, in principle, destroys such an effect. Microscopic symmetry roughening is not destroyed in the presence of a mother phase.

The inversion plays a special role. It was not mentioned in §3.4.3 because there inhomogeneous symmetry elements and $P\bar{1}$, which is symmorphic, were treated. If one considers, however, a space group like *Pnnn*, then, depending on the choice of the origin, the inversion has a non-primitive translation $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. For such a space group, any face normal $\mathbf{k}_{hkl}$ is invariant under the inversion up to a sign and the non-primitive translation ensures the presence of a doublet with height difference as long as the inversion is not at a special position of the connected net.

The effect of symmetry on crystal morphology has been treated in this paper on a microscopic scale without taking the actual growth mechanism into account. Microscopic growth mechanisms such as spiral growth are also symmetry determined. An example of such microscopic effects on interlacing as observed for spirals on crystals of *e.g.* SiC and $NiSO_4 \cdot 6H_2O$ will be treated by van Enckevort & Bennema (1998).

7. Conclusions

In this paper, all possible symmetries in crystals where symmetry roughening of pairs of connected nets can take place are deduced. The relevant symmetries are those that leave the orientation of the face unchanged up to a sign. Within this catagory of symmetry elements, one can distinguish three situations:

symmetry elements that leave the connected net invariant (singlet);

symmetry elements that relate a doublet covered by the well established Bravais–Friedel–Donnay–Harker (BFDH) rules;

doublets that can cause symmetry roughening.

Singlets have no restriction and BFDH doublets result in selection rules that are the same as the general reflection conditions used in X-ray crystallography. When a pair of connected nets of the same face (*hkl*) obeying the BFDH conditions is related by symmetry, the face, in principle, gets rough when no alternative singlet is present. This does not always mean that the corresponding face (*hkl*) also becomes rough on a macroscopic scale.

An important distinction is made between microscopic and macroscopic roughening. If the pairwise symmetric connected nets are at a different height as seen along the face normal, then the face becomes rough macroscopically, that is, gets rounded off if there is no alternative singlet connected net present. According to the definition of an *F* face given in paper I, such a face is not an *F* face.

If the nets are at the same height, the face does not get rounded off but it always becomes rough microscopically unless there is an alternative connected net present. The alternative nets that can destroy symmetry roughening must contain bonds parallel to the face.

The presence of a mother phase does not alter these cases as long as the symmetry element does not invert the boundaries of the connected nets, that is, as long as there is no boundary swapping. In the case of boundary swapping, the pair does not get rough if the symmetry element is at a special position of the connected net. In such a case, the net is non-polar. If the boundary swapping occurs for a more general position of the symmetry element and a mother phase is present, the interaction with the mother phase can destroy the symmetry roughening. All these situations are summarized in Table 1.

It is clear that symmetry roughening can have severe implications for the morphology of crystals. First of all, the morphological importance of a face can be reduced drastically because a pair of connected nets of the face can get rough owing to symmetry roughening leaving a weaker alternative connected net behind. If there is no alternative, the face will not show up at all or is rounded off for macroscopic symmetry roughening. In the case of microscopic symmetry roughening, the face stays macroscopically flat.

One of the questions that arise is whether the growth mechanism of microscopically rough faces is different from that of normal faces. Another point to be studied is the effect of a finite temperature or a finite supersaturation. One can imagine that a pair of connected nets that is not exactly symmetry related but just differs slightly in bond energies will still become rough at a finite temperature or supersaturation. In such a case, one could speak of thermal symmetry roughening or kinetical symmetry roughening, respectively, or, more generally, of pseudo symmetry roughening. In practice, one frequently encounters crystals with pairs of connected nets that, though structurally clearly not related by symmetry, have very comparable bond energies. On the other hand, a mother phase interacting with the crystal surface could cause only a small energy difference for a pair of connected nets in the case of boundary swapping. In such a case, the discriminating effect of the mother phase can be destroyed by a finite superstaturation. Again, the implications of a nonequilibrium situation can have severe implications for the morphology. Such situations will be put in a broader perspective of morphological importance of faces in paper III of this series (Grimbergen, Bennema & Meekes, 1998).

The effect of a mother phase interacting with the crystal surface has been neglected very often in the past. In this paper and paper I, the influence of the symmetry of connected nets in the boundary between crystal and mother phase is explicitly taken into account. Further studies into this matter including modelling studies will become more and more achievable using modern computing power and modelling software. In such studies, the implication of symmetry roughening and in particular pseudo symmetry roughening are expected to become apparent, offering a more reliable tool to predict crystal morphology using periodic bond chain analysis.

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