

## On the Prediction of Crystal Morphology. I. The Hartman–Perdok Theory Revisited

R. F. P. GRIMBERGEN, H. MEEKES,\* P. BENNEMA, C. S. STROM AND L. J. P. VOGELS†

*RIM Laboratory of Solid State Chemistry, Faculty of Science, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands. E-mail: hugom@sci.kun.nl*

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Dedicated to P. Hartman

### Abstract

The over 40 year old Hartman–Perdok (HP) [Hartman & Perdok (1955). *Acta Cryst.* **8**, 49–52, 521–524, 525–529] theory for predicting crystal morphology is reconsidered. The new approach, which gives a physical foundation to the theory, is based on  $F$  faces having a roughening transition temperature higher than 0 K. The aim of this paper is to confront the field of crystal growth and in particular the classical HP theory with modern statistical thermodynamical treatments of models of surfaces of relatively simple crystal structures. It is shown that crystal faces ( $hkl$ ) containing multiple connected nets with a relatively high energy content may have a very low roughening temperature and an unexpectedly high growth rate. In some cases, crystal faces become rough at 0 K because of multiple connected nets related by symmetry giving rise to symmetry roughening. The use of connected nets in the HP theory offers the possibility of extrapolating the results of statistical thermodynamical models of simple crystal surfaces to more complex crystals as encountered in practice. The role of the step free energy in understanding crystal morphology is emphasized.

### 1. Introduction

In 1951, Burton, Cabrera & Frank published a famous paper about the growth of crystals and the equilibrium structure of their surfaces. They introduced the spiral growth mechanism for imperfect crystals to the already known two-dimensional nucleation mechanism for perfect-crystal surfaces. Furthermore, they discussed the phenomenon of surface roughening using the two-dimensional statistical thermodynamical models of Onsager (1944).

A few years later, Hartman & Perdok (1955*a,b,c*) formulated the Hartman–Perdok (HP) theory, also known as the periodic bond chain (PBC) theory, for deriving the crystal morphology from the crystal structure. Hartman & Perdok did not explicitly take the

effect of surface phase transitions, like the roughening transition, into account.

Since Onsager (1944), statistical thermodynamical surface models have become applicable to more complex crystal surfaces and many surface phases like the normal flat, reconstructed flat, disordered flat (DOF) and rough phase have been found (Leamy & Gilmer, 1974; van Beijeren, 1977; Rommelse & den Nijs, 1987; den Nijs & Rommelse, 1989; Mazzeo *et al.*, 1995). Nevertheless, many practically grown crystals are too complex to describe with an accurate statistical thermodynamical model.

In this paper, it will be shown that integration of the crystallographic HP theory and statistical thermodynamical surface models can be used to derive the equilibrium and growth morphology qualitatively, and in many cases quantitatively, of a very wide range of crystals. For this, the  $F$  face defined by Hartman & Perdok will be redefined as a crystal face having a roughening temperature higher than 0 K.  $F$  faces can be determined from a crystal structure by determination of all connected nets. Analysis of all connected nets for a single orientation ( $hkl$ ) in terms of relatively simple statistical thermodynamical surface models yields information about the equilibrium and the growth behaviour of the specific face. It will be shown that certain combinations of connected nets cause an unexpectedly high growth rate when the step energy is very small. As a special case of the latter, combinations of symmetry-related connected nets may result in a zero step energy. These situations give rise to symmetry roughening.

The paper is organized as follows. First, a historical overview of morphological theories is given in which the HP theory and the statistical thermodynamical theory of roughening transitions are emphasized. Next, in §3 an  $F$  face will be redefined and the relation between connected nets and statistical thermodynamical models of interface roughening will be explained. Symmetry of connected nets in the broken-bond description and the influence of a mother phase taking the crystal symmetry and destruction of symmetry into account will be treated in §4. We end with a *Discussion and conclusion*.

† Present address: MOS4YOU, Philips Semiconductors, Gerstweg 2, 6534 AE Nijmegen, The Netherlands.

## 2. History of crystallography and morphology

### 2.1. Bravais, Friedel, Donnay and Harker (BFDH)

The science of crystallography started when Haüy discovered the law of rational indices (Haüy, 1792). From a modern point of view, this law can be stated as follows: Faces occurring on crystals are parallel to net planes that are perpendicular to a reciprocal-lattice vector:

$$\mathbf{k}(hkl) = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \quad h, k, l \in \mathbb{Z}. \quad (1)$$

Here,  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  are the reciprocal-lattice vectors. Only the orientation of a face occurring on a crystal is relevant. This orientation is adequately described by three integers  $(hkl)$ , which are prime in reference to each other. In the period 1880 to 1939, the following law of the relative morphological importance of faces  $(hkl)$  was formulated by Bravais, Friedel, Donnay and Harker (this is called nowadays the BFDH law). The larger the interplanar distance  $d_{hkl}$ , the larger the MI (morphological importance) of  $(hkl)$  or

$$d_{h_1k_1l_1} > d_{h_2k_2l_2} \rightarrow \text{MI}_{h_1k_1l_1} > \text{MI}_{h_2k_2l_2}. \quad (2)$$

The MI of a face  $(hkl)$  is defined as the relative statistical frequency of occurrence of the face  $(hkl)$  or the relative size of the face  $(hkl)$  occurring on a set of crystals of a certain compound. According to Bravais and Friedel, the values of  $d_{hkl}$  ought to be corrected for non-primitive cells if these cells are used to calculate  $d_{hkl}$ 's (Friedel, 1911). These corrections may lead to integers  $h$ ,  $k$  and  $l$  that are mutually non-prime. According to Donnay & Harker (1937),  $d_{hkl}$ 's need to be corrected for screw axes and glide planes of the space group of the crystal structure because exactly the same crystal surfaces are separated by  $d_{nhknkl}$  with  $n \in \mathbb{N}$ . An intuitive extension of the Donnay-Harker law was given by Donnay & Donnay (1961) for the case that surfaces separated by  $d_{nhknkl}$  are almost exactly the same.

In general,  $d_{hkl}$  has, at least, to be corrected by the crystallographic selection rules as given in *International Tables for X-ray Crystallography* (1969). For a treatment of the BFDH law, see Hartman (1973, 1978). In order to

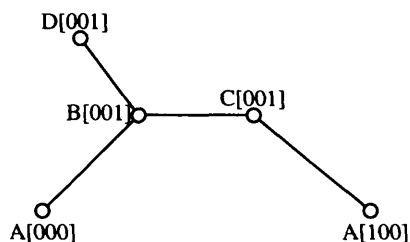


Fig. 1. Schematic drawing of a PBC with an overall translation  $[100]$  consisting of growth units  $A[000]$ ,  $B[001]$ ,  $D[001]$ ,  $C[001]$  and  $A[100]$ . The  $DC[100]$  consists of  $A[000]$ ,  $B[001]$ ,  $C[001]$  and  $A[100]$ . The chemical composition of the crystal is  $ABCD$ . Note that growth unit  $D$  is not needed to connect  $A[000]$  with  $A[100]$ .

get an impression of how crystal (growth) forms look, according to the BFDH law, the *ad hoc* assumption may be introduced that the relative growth rate  $\mathbf{R}_{hkl}$  of faces  $(hkl)$  is inversely proportional to  $d_{hkl}$  or proportional to  $k = |\mathbf{k}_{hkl}|$ . Plotting vectors with a length  $R = |\mathbf{R}_{hkl}|$  from an origin and erecting faces  $(hkl)$  perpendicular to the vectors  $\mathbf{R}_{hkl}$ , a crystal form is obtained. Using this so-called Wulff construction (Wulff, 1901), crystal forms are obtained, which are dominated by faces  $(hkl)$  with the highest  $d_{hkl}$  and thus the smallest  $|\mathbf{k}_{hkl}|$ . If the space group and elementary cell of a given structure are known, all  $d_{hkl}$  values can be calculated and crystal forms can be constructed.

### 2.2. Hartman-Perdok theory

The BFDH law often gives a satisfactory description of the morphology of crystals. There are, however, striking discrepancies between predicted and observed morphologies. The drawback of the BFDH law is its purely geometrical character. Neither the real crystal structure nor the concept of chemical bond and statistical thermodynamics of interfaces or crystal-growth mechanisms are taken into account. In 1955, Hartman & Perdok published three papers, which can be considered as a breakthrough in the theory of morphology, a subsience of crystal growth theory (Hartman & Perdok, 1955a,b,c). In the original HP theory, the concept of periodic bond chain (PBC) plays a key role. A PBC is an uninterrupted chain of bonds representing strong interactions between growth units with an overall periodicity  $[uvw] = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$  ( $u, v, w \in \mathbb{Z}$ ) of the direct primitive lattice and contains no other lattice translation. Moreover, a PBC is stoichiometric with regard to the unit-cell contents. In the classical HP theory, three types of faces were distinguished:

$F$  faces parallel to at least two non-parallel intersecting PBCs

$S$  faces parallel to only one PBC

$K$  faces not parallel to any PBC.

Owing to the periodicity of the structure, two PBCs constituting an  $F$  face determine the composition of an  $F$  slice parallel to  $(hkl)$ .

Strom has developed a computer program for automatic derivation of  $F$  slices. She has shown that it is conceptually more simple and computationally more straightforward to derive the  $F$  slices by determining and combining direct chains (DCs) instead of PBCs (Strom, 1985). A direct chain is defined as a sequence of strongly bonded growth units of which only the end points are identical (*i.e.* related by a lattice translation) (Strom, 1980). In contrast to PBCs, DCs need not be stoichiometric with regard to the chemical composition of the crystal (see Fig. 1). Note that each PBC consists of at least one DC and that a stoichiometric DC is also a PBC.

$F$  slices can be considered as growth layers or surface configurations. In order to determine which surface

configuration will be most pronounced on the growth form in the absence of external factors, often the slice energy values associated with the various  $F$  slices in  $(hkl)$  are calculated.

Within the framework of the HP theory, it is assumed [and this can be justified (Hartman & Bennema, 1980)] that the rate of growth  $R_{hkl}$  of a face  $(hkl)$  increases with the attachment energy. This implies that for two faces  $(h_1k_1l_1)$  and  $(h_2k_2l_2)$  the following relation holds:

$$|E_{h_1k_1l_1}^{\text{att}}| > |E_{h_2k_2l_2}^{\text{att}}| \rightarrow R_{h_1k_1l_1} > R_{h_2k_2l_2}. \quad (3)$$

Quite often, in order to get an impression of the habit of crystals, the *ad hoc* assumption is introduced that  $R_{hkl}$  is proportional to  $|E_{hkl}^{\text{att}}|$  or

$$R_{hkl} = CE_{hkl}^{\text{att}}. \quad (4)$$

Here  $C$  is a constant.  $E_{hkl}^{\text{att}}$  is defined as the energy released per growth unit when a complete growth layer is attached to a surface  $(hkl)$ . It is complementary to  $E_{hkl}^{\text{slice}}$ .  $E_{hkl}^{\text{att}}$  and  $E_{hkl}^{\text{slice}}$  together give the crystallization energy  $E^{\text{cr}}$  or

$$E^{\text{cr}} = E_{hkl}^{\text{att}} + E_{hkl}^{\text{slice}}. \quad (5)$$

It follows that crystals will be, in principle, bounded by  $F$  slices having the lowest  $R_{hkl}$  or the lowest  $|E_{hkl}^{\text{att}}|$  and the highest  $|E_{hkl}^{\text{slice}}|$  (Hartman & Perdok, 1955a,b,c; Hartman & Bennema, 1980; Hartman, 1973, 1987). Faces  $(hkl)$  with the highest  $|E_{hkl}^{\text{slice}}|$  will also have in most cases the largest  $d_{hkl}$ . This explains the success of the BFDH law (Hartman, 1978). The HP theory has been applied with great success to numerous crystalline structures both organic and inorganic (Hartman, 1987; Bennema & van der Eerden, 1987; Bennema, 1993). The theory was extended to ionic crystals and Madelung and Ewald methods were used to calculate  $E_{hkl}^{\text{att}}$  and  $E_{hkl}^{\text{slice}}$  (Hartman, 1987; Bennema & van der Eerden, 1987; Woensdregt, 1990; Strom & Hartman, 1989).

### 2.3. Equilibrium forms and growth forms

The theory of equilibrium forms, firmly rooted in thermodynamics, leads to a logical recipe to construct an equilibrium form. This recipe is given by (Wulff, 1901; Herring, 1953)

$$D_{hkl} = A\sigma_{hkl}, \quad (6)$$

where  $D_{hkl}$  is the distance from the origin of the coordinate system to the face  $(hkl)$ . It is proportional to the surface free energy  $\sigma_{hkl}$  ( $A$  is a constant) of the face. An equilibrium form can be obtained using the Wulff construction. A review on equilibrium forms is given by Kern (1987).

In order to obtain growth forms, in equation (6),  $\sigma_{hkl}$  has to be replaced by the relative growth rates  $R_{hkl}$ . Expressions for  $R_{hkl}$  may be given by  $R_{hkl} \propto (d_{hkl})^{-1}$ ,  $R_{hkl} \propto E_{\text{att}}$  or more sophisticated expressions derived

from the modelled fluid part of the interface and kinetic crystal growth models (Liu *et al.*, 1995a,b).

The spread in growth rates of experimentally observed crystals even of symmetrically equivalent faces (of one form  $\{hkl\}$ ) may be very high owing to different growth histories of different faces caused by different dislocations, hydrodynamics or absorption of impurities.

### 2.4. Theory of roughening transition

In the 1950s, Burton, Cabrera & Frank described the transition of flat crystal faces at equilibrium to roughened faces as a function of temperature (Burton *et al.*, 1951). At that time, an exact calculation of the roughening transition was restricted to a rectangular two-dimensional lattice with equal or different interactions in the two crystallographic directions (Onsager, 1944). The allowed height differences in this model were  $|\Delta h| \pm 1$  (unit cell). For this model, the step free energy decreases linearly with increasing temperature  $T$  and vanishes at  $T = T^C$ , the transition temperature. This type of surface transition is known as the Ising transition.

The theory of roughening transitions was developed further in the 1970s by Kosterlitz & Thouless (1973, 1974), Leamy & Gilmer (1974), van Beijeren (1977), Swendsen (1978), Müller-Krumbhaar (1978) and Shugard *et al.* (1978). For these models, the height differences  $\Delta h$  were not restricted to  $|\Delta h| \pm 1$ . It was shown that the cubic faces of a simple cubic solid-on-solid (SOS) model and the body-centred solid-on-solid (BCSOS) model show a roughening transition of infinite order, which is characterized by a critical (dimensionless) temperature  $\theta_{hkl}^R$  such that

$$\begin{aligned} \theta < \theta_{hkl}^R &\rightarrow \gamma_{hkl} > 0 \\ \theta \geq \theta_{hkl}^R &\rightarrow \gamma_{hkl} = 0, \end{aligned} \quad (7)$$

where  $\gamma_{hkl}$  represents the step free energy of a step on the face  $(hkl)$ . The dimensionless roughening temperature for a face  $(hkl)$  is defined by

$$\theta_{hkl}^R = 2kT_{hkl}^R/\Phi_{\text{str}}, \quad (8)$$

where  $\Phi_{\text{str}}$  represents an arbitrary reference bond which in this case is the strongest bond of the crystal and the factor 2 is conventional.  $T_{hkl}^R$  is the absolute roughening temperature of the face  $(hkl)$ . It was shown that for these models the step free energy  $\gamma$  vanishes continuously as

$$\gamma \simeq \exp[-\alpha(T^R - T)^{-1/2}], \quad T \leq T^R, \quad (9)$$

where  $T$  is the actual temperature and  $\alpha$  is a coefficient depending on the system. In general, the roughening temperature  $T^R$  is somewhat higher than the Ising transition temperature  $T^C$ .

The bond energies at the interface have within the framework of cell models the shape (Bennema & van

der Eerden, 1987; Bennema, 1993, 1996)

$$\Phi_i = \Phi_i^{sf} - \frac{1}{2}(\Phi_i^{ss} + \Phi_i^{ff}), \quad (10)$$

where *sf* refers to a solid–fluid bond, *ss* to a solid–solid bond and *ff* to a fluid–fluid bond. Fluid means, here, any mother phase, including a very dilute vapour.  $\Phi_i$  corresponds to the broken-bond energy of the *i*th bond of the crystal.

As shown above, the concept of roughening transition was derived for simple crystals like the simple cubic SOS and BCSOS models. For real crystal faces simplified to somewhat more complex Kossel-like structures, van der Eerden (1976), Rijpkema *et al.* (1982) showed that the two-dimensional Ising transition temperature  $T_{hkl}^C$  may be used as an (usually lower bound) estimate for the roughening temperature  $T_{hkl}^R$ .

We note that during the past ten years a lot of effort has been put into understanding complex interface models from a statistical thermodynamical point of view. Rommelse and den Nijs found a pre-roughening transition to a so-called disordered flat (DOF) phase with next-nearest-neighbour interactions (Rommelse & den Nijs, 1987; den Nijs & Rommelse, 1989). Mazzeo *et al.* (1995) calculated a phase diagram for the two-component BCSOS model. The latter phase diagram, which is applicable to caesium chloride type structures, exhibits flat, reconstructed flat, disordered flat and rough phases.

The implication of the roughening transition for crystal faces (*hkl*) is that these faces will, in essence, remain flat in thermodynamic equilibrium at a temperature below the roughening temperature. Even if this surface is exposed to a driving force for crystallization, the surface will grow by a layer mechanism (two-dimensional nucleation or spiral growth) keeping in principle the orientation (*hkl*). Note that a crystal face may become rough below the roughening temperature because of a high driving force. This phenomenon is known as kinetic roughening (Elwenspoek & van der Eerden, 1987; Jetten *et al.*, 1984). If in equilibrium the surface has a temperature above its roughening temperature, it will no longer keep its orientation (*hkl*) and, in the case of growth, it will grow as a macroscopically rounded-off surface without orientation (*hkl*). This is because the step free energy has become zero.

It has been shown by Prestipino *et al.* (1995) that the disordered flat phase may have major implications for the growth behaviour of crystal faces.

### 3. Derivation of *F* faces based on crystallography and the concept of roughening

In this section, a new definition for an *F* face will be given based on the concept of roughening. Using a

model crystal graph, it will be shown that specific combinations of connected nets result in very low or even zero step energy. This may have major implications for the equilibrium and growth behaviour of a crystal face (*hkl*).

#### 3.1. Definition of an *F* face

In the HP theory, the definition of an *F* face still includes faces that, despite the presence of two intersecting non-parallel PBCs, have a roughening temperature of 0 K. In order to include such cases, we will use a definition of an *F* face based on the theory of roughening transition. An *F* face (*hkl*) is defined as a crystal face (*hkl*) with a roughening temperature larger than 0 K ( $T_{hkl}^R > 0$  K).

van Beijeren & Nolden (1986) have shown that a flat face (*i.e.* a crystal face below the roughening temperature) with normal  $\mathbf{k}$  has the property that for all crystallographic directions  $\mathbf{u} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$  labelled by [*uvw*] ( $u, v, w \in Z$ ) coplanar with the face (*i.e.*  $\mathbf{u} \cdot \mathbf{k} = 0$ ), the sum of the step free energies of a step in the  $\mathbf{u}$  and  $-\mathbf{u}$  directions is larger than zero, or

$$\gamma(\mathbf{u}) + \gamma(-\mathbf{u}) > 0 \quad \forall \mathbf{u}, \mathbf{u} \cdot \mathbf{k} = 0. \quad (11)$$

If one wants to predict and understand crystal morphology and crystal growth, one has to determine all *F* faces (*i.e.* crystal faces with  $T^R > 0$ ) from the crystal structure. As argued before, it is almost impossible for practical crystals to determine all these faces on the basis of statistical thermodynamic models. A convenient solution to this problem is to derive all connected nets of a crystal structure and subsequently analyse these on the basis of relatively simple statistical thermodynamic models.

A connected net is defined as the combination of at least two intersecting non-parallel direct chains (DCs). Equivalent connected nets are separated by the interplanar distance  $d_{hkl}$  according to the BFDH law. This is the distance that separates physically identical surfaces. All equivalent growth units in all DCs constituting a connected net differ by a translation  $\mathbf{u}$  perpendicular to  $\mathbf{k}$ . This is called the flatness criterion.

Note that there is a difference between a connected net and an *F* slice defined earlier by Strom. She defined an *F* slice as the combination of at least two intersecting non-parallel PBCs (Strom & Heijnen, 1981). All equivalent growth units in all PBCs constituting an *F* slice differ by a translation  $\mathbf{u}$  perpendicular to  $\mathbf{k}$  (flatness criterion). The definition implies that the *F* slices are stoichiometric with respect to the chemical composition of the unit cell. In contrast, connected nets need not be stoichiometric. A further difference between the HP theory and the present approach is that Hartman (1973) does not allow polar *F* slices for centrosymmetric crys-

tals whereas polar connected nets are allowed in the present analysis.

For the determination of connected nets from a crystal structure, it is convenient to reduce growth units in the crystal lattice to their geometrical centres (or centres of gravity if preferred) and represent strong interactions between the growth units by bonds between these centres. In this way, an infinite set of points connected with bonds to each other is formed. Inspired by graph theory, we define this as the crystal graph. It must be emphasized that in general the crystal graph has a higher symmetry than the corresponding crystal. In all cases, the actual space-group symmetry of the crystal has to be considered.

The proposed model crystal graph is presented in Fig. 2. Note that for clarity we have drawn more than the unit cell. The crystal graph consists of two types of growth units *A* and *B*, which are indicated by their centres of gravity. The stoichiometry of the crystal is *AB*. Growth units *A* are situated at the corners and growth units *B* in the centre of the elementary cell. Note that the actual positions of the growth units in the crystal can have a lower symmetry. Between growth units *A* and *B* bonds *c* and *d* are present. In the [100] and [010] directions, two neighbouring growth units *A* are connected to each other by the bonds *a*. In the same way, two adjacent growth units *B* are connected by bonds *b* in the [100] and [010] directions.

In the discussion of different types of *F* faces, different crystal graphs will be derived from the model

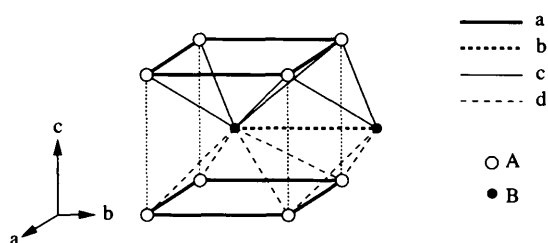


Fig. 2. Basic model crystal graph. The *b* bond is present in both the [100] (not drawn) and [010] directions.

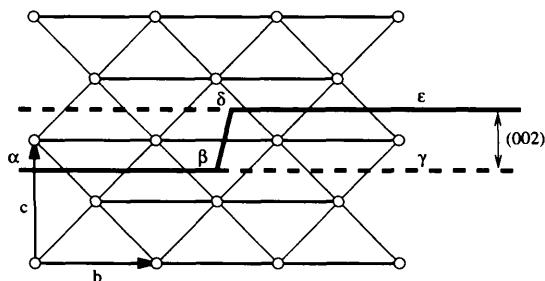


Fig. 3. [100] projection of the (001) face of the crystal graph of Fig. 2 with  $b = a$ ,  $d = c$  and  $B = A$ . The indicated step along [010] is equivalent to a step along [100].

crystal graph in Fig. 2 by redefining the *a*, *b*, *c* and *d* bonds and growth units *A* and *B*.

### 3.2. Discussion of connected nets and *F* faces

In the following, some properties of *F* faces and connected nets will be explained and illustrated using the model crystal graph depicted in Fig. 2.

For simplicity, all bond energies used in the analysis are so-called broken-bond energies, which are defined as the energy needed to break the bond between the growth units. Thus, per growth unit, the broken-bond energy is half the bond energy of the bond between two growth units. In the following, step energies will be calculated on the basis of these broken bonds. Therefore, step energies instead of step free energies are used. Such an approach can still be used to determine whether a face is an *F* face as the entropy contribution to the free energy is zero at 0 K.

The broken-bond energies of the bonds *a*, *b*, *c* and *d* will be indicated by  $\Phi_a$ ,  $\Phi_b$ ,  $\Phi_c$  and  $\Phi_d$ , respectively. It is assumed that there are no other interactions in the crystal lattice apart from the bonds defined in the crystal graph. The effect of long-range interactions, surface relaxations, polarity and crystal-mother-phase interactions will be ignored at this stage but will be discussed in §4.

#### 3.2.1. Illustration of the BFDH law for connected nets.

Consider the crystal graph of Fig. 2 with  $b = a$ ,  $d = c$  and  $B = A$ . The [100] projection of the (001) face is shown in Fig. 3. The unit cell is an *I*-centred cell. Application of the BFDH law will result in a halving of the interplanar distance separating exactly equivalent surfaces. In that case, there is a single connected net (002) presented in Fig. 3. The step energy for the orientation (001) can be calculated comparing the surface energies of a flat surface bounded by  $\alpha\beta\gamma$  with the surface energy of a surface with a step bounded by  $\alpha\beta\delta\epsilon$ . Counting the broken bonds results in a step energy of  $\Phi_a$ . This illustrates the law of Bravais and Friedel for non-primitive cells. The general BFDH law is illustrated by the same figure if it were the crystal graph of the crystal of Fig. 2 with space-group symmetry  $P112_1$ .

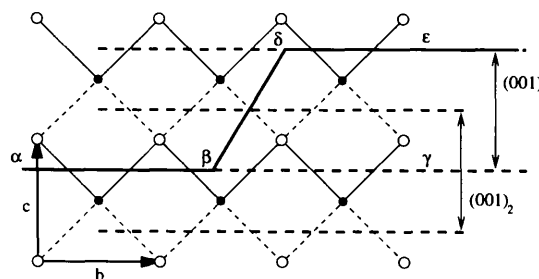


Fig. 4. [100] projection of the crystal graph of Fig. 2 without *a* and *b*. The indicated step along [010] is equivalent to a step along [100].

Under growth conditions ( $\Delta\mu > 0$ ), this type of crystal face will grow with layers of thickness  $d_{002}$  at a temperature below the roughening temperature ( $T < T^R$ ) and at a low driving force not causing kinetic roughening.

**3.2.2. Multiple connected nets.** Consider the (001) face of the crystal graph in Fig. 2 with  $\Phi_a = \Phi_b = 0$ . In this case, two different connected nets (001)<sub>1</sub> and (001)<sub>2</sub> are present as indicated in Fig. 4. The step energy can be calculated by taking the difference in surface energy for (001)<sub>1</sub> between the surface bounded by  $\alpha\beta\gamma$  and the surface bounded by  $\alpha\beta\delta\epsilon$  as equal to the difference in bond energy  $2(\Phi_d - \Phi_c)$ . As a result, the roughening temperature for the *F* face (001) is larger than 0 K. At equilibrium conditions, the face would be flat and bounded by the surface with the lowest surface energy. If the *c* bond is stronger than the *d* bond, the surface would be bounded by the *A* growth units. Under growth conditions ( $\Delta\mu > 0$ ) at a temperature  $T < T^R$ , the surface would then grow with layers (001)<sub>2</sub>.

In Fig. 5, the [100] projection of the (001) face of the model crystal graph of Fig. 2 is drawn, now including all bonds. For this orientation, four-connected nets indicated by (001)<sub>1</sub>, (001)<sub>2</sub>, (001)<sub>3</sub> and (001)<sub>4</sub> can be found. The connected nets (001)<sub>1</sub> and (001)<sub>2</sub> each consist of the two connected nets (001)<sub>3</sub> and (001)<sub>4</sub>. If (001)<sub>1</sub> represents the preferred surface configuration, the step energy can be calculated, as shown before, by calculation of the surface-energy difference between interfaces  $\alpha\beta\gamma$  and  $\alpha\beta\delta\epsilon$ . In this case, the step energy is equal to  $(2\Phi_d - 2\Phi_c) + \Phi_a + \Phi_b$ .

For growth below the roughening temperature, the crystal will grow layer by layer preferring the lowest energy surface at the interface. Assuming that  $\Phi_c < \Phi_d$ , the crystal will grow with layers (001)<sub>1</sub>. Under certain conditions, it is more favourable to grow effectively with half layers by alternating layers (001)<sub>3</sub> and (001)<sub>4</sub>. The growth behaviour of faces containing multiple connected nets will be the subject of a future paper (Grimbergen, Bennema & Meeke, 1998).

**3.2.3. Symmetry roughening.** We now consider a limiting case of the (001) face as presented in Fig. 4 for which  $\Phi_a = \Phi_b = 0$  and  $c = d$ . Note that still growth unit *A* differs from growth unit *B*. A [100] projection of the crystal graph is shown in Fig. 6. Again, two different connected nets can be distinguished, indicated by (001)<sub>1</sub>

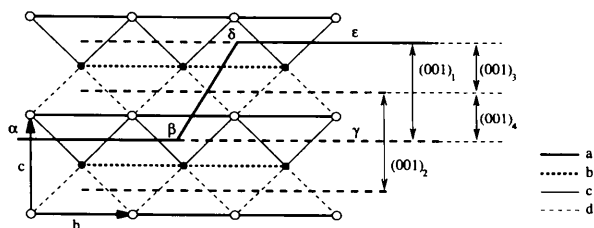


Fig. 5. [100] projection of the (001) face of the crystal graph of Fig. 2. The indicated step along [010] is equivalent to a step along [100].

and (001)<sub>2</sub>. The topology of the two connected nets is identical but the difference is that for (001)<sub>1</sub> *B* growth units while for (001)<sub>2</sub> *A* growth units are at the surface. In Fig. 6, it can be seen that, starting from a surface with *B* on top, the difference in broken-bond energy of a flat surface bounded by  $\alpha\beta\gamma$  and a surface with one step bounded by  $\alpha\beta\delta\epsilon$  is equal to zero resulting in a zero step energy. This implies that this face would be rough at 0 K ( $T^R = 0$ ). The same holds if one starts with the *A* growth units on top. This special situation will be referred to as *symmetry roughening*. Symmetry roughening will be treated extensively in a forthcoming paper (Meeke *et al.*, 1998).

If the unit cell is an *I*-centred cell and consequently  $A = B$ , there would not be a valid connected net for the face (001). This is trivial because the layer thickness  $d_{001}$  would become  $d_{002}$  according to the crystallographic BFDH law and there are no connected nets (002) (see Fig. 6). The consequence is that the face would be rough at  $T = 0$  K and thus not be a valid *F* face. This has also been found for the body-centred solid-on-solid (BCSOS) model. For the BCSOS model without next-nearest-neighbour interactions, the roughening temperature of the (001) face is 0 K (van Beijeren, 1977).

**3.2.4. Illustration of equation (11).** In some specific cases, the step energy for a step in a direction  $\mathbf{u}$  may not be equivalent to a step in the opposite direction  $-\mathbf{u}$ . This is illustrated in Fig. 7. The *c* and *d* bonds have been divided into  $c_1, c_2, d_1$  and  $d_2$  bonds.

Two connected nets can be distinguished indicated with (001)<sub>1</sub> and (001)<sub>2</sub>. Calculation of the step energy for the step  $\alpha\beta\gamma\delta$  on the (001)<sub>1</sub> face yields  $(2\Phi_{d_2} - 2\Phi_{c_2})$  and for the step  $\kappa\epsilon\delta\gamma$   $(2\Phi_{d_1} - 2\Phi_{c_1})$ . Assuming that  $(\Phi_{c_1} + \Phi_{c_2}) < (\Phi_{d_1} + \Phi_{d_2})$ , different situations may occur:

$$\begin{aligned} &(\Phi_{c_1} < \Phi_{d_1}) \wedge (\Phi_{c_2} < \Phi_{d_2}); \\ &(\Phi_{c_1} > \Phi_{d_1}) \wedge (\Phi_{c_2} < \Phi_{d_2}); \\ &(\Phi_{c_1} < \Phi_{d_1}) \wedge (\Phi_{c_2} > \Phi_{d_2}). \end{aligned}$$

In the first case, both step energies are positive. In the second situation, the step energy for the step  $\alpha\beta\gamma\delta$  is positive while the step energy for the step  $\kappa\epsilon\delta\gamma$  is negative! The third situation corresponds to the reverse. In all situations mentioned, relation (11) holds. There-

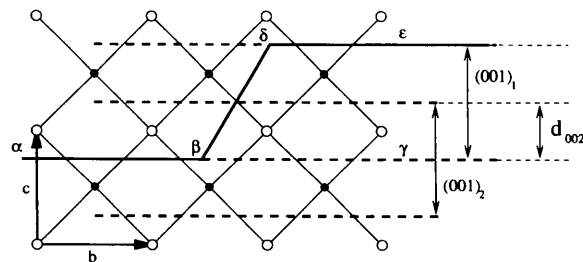


Fig. 6. [100] projection of the (001) face of the crystal graph of Fig. 2 with  $a = b = 0$  and  $c = d$ . A step along [100] is equivalent to the indicated step [010].

fore, the face is a genuine  $F$  face having a roughening temperature larger than 0 K. Obviously, the face would become rough when  $(\Phi_{c_1} + \Phi_{c_2}) = (\Phi_{d_1} + \Phi_{d_2})$ . If  $(\Phi_{c_1} + \Phi_{c_2}) > (\Phi_{d_1} + \Phi_{d_2})$ , the  $(001)_2$  connected net would give the surface configuration with the lowest surface energy.

### 3.3. Disordered flat faces

For some time, interface models were based on first-nearest-neighbour bonds and it has been shown that some specific models like the SOS, RSOS and BCSOS models (Leamy & Gilmer, 1974; van Beijeren, 1977; Swendsen, 1978; Müller-Krumbhaar, 1978; Shugard *et al.*, 1978) show a roughening transition. Later, Rommelse and den Nijs found a new phase of crystal surfaces, a so-called disordered flat (DOF) phase by taking next-nearest-neighbour interactions into account (Rommelse & den Nijs, 1987; den Nijs & Rommelse, 1989). In their model, this phase occurs intermediate between the flat and the rough phases of a crystal face.

In our description of crystal faces based on connected nets, the DOF phase can also be identified. This can be illustrated looking at Fig. 8. If the bonds  $c$  and  $d$  are considered as first-nearest-neighbour solid-on-solid bonds and the  $a$  and  $b$  next-nearest-neighbour bonds are not equivalent ( $\Phi_a \neq \Phi_b$ ), this model is identical to the staggered BCSOS model described by Mazzeo *et al.* (1995) for which the phase diagram is known and a disordered flat phase has been identified. Apart from the connected nets  $(001)_1$  and  $(001)_2$ , two connected nets  $(001)_3$  and  $(001)_4$  can be identified. Of the latter two connected nets, each has its own two-dimensional Ising transition temperature  $T_{(001)_3}^C$  and  $T_{(001)_4}^C$ , respectively. In Fig. 8, it can be seen that the step energy for this crystal face is  $(\Phi_a + \Phi_b)$  independent of whether connected net  $(001)_1$  or connected net  $(001)_2$  is chosen as surface configuration. This is a consequence of the broken-bond description. Thus, the crystal face will have a roughening temperature higher than 0 K.

At temperatures lower than the Ising temperatures of the two individual connected nets  $(001)_3$  and  $(001)_4$ , the surface will be flat. For the moment it will be assumed that  $\Phi_a > \Phi_b$  and consequently  $T_{(001)_3}^C < T_{(001)_4}^C$ . When the temperature becomes higher than the two-dimensional Ising temperature of the  $(001)_3$  connected net  $[(T > T_{(001)_3}^C) \wedge (T < T_{(001)_4}^C)]$ , the crystal face will show an

Ising transition to a DOF phase. Consequently, the crystal face will be essentially flat because of the connected net  $(001)_4$  with the highest Ising temperature. However, the  $(001)_3$  connected net will not be ordered any more. When the temperature is increased further ( $T > T_{(001)_3}^R$ ), one would expect the crystal face to show a roughening transition from the DOF phase to a rough phase. However, it was proven for the two-component BCSOS model that there is no roughening transition and the crystal face will stay in the DOF phase as long as  $\Phi_a \neq \Phi_b$  (Mazzeo *et al.*, 1995). This behaviour may be due to the strict BCSOS condition of the model (van Beijeren & Nolden, 1986). For real crystals, such types of faces will probably have a roughening transition at higher temperatures.

The implication for crystal morphology is that flat and DOF phases will result in well defined flat crystal facets on a macroscopic scale, while a rough face would be observed as a macroscopically rounded-off face. Furthermore, a DOF phase may result in anomalous growth behaviour compared with a normal flat face. Prestipino *et al.* (1995) have shown for the FCSOS model, using Monte Carlo simulations, that exactly at the pre-roughening temperature the crystal face grows continuously and has a very high growth rate, whereas just above and below this critical temperature the crystal grows layer by layer and the growth rate is lower.

### 3.4. Reconstructed flat faces

The connected-net analysis is principally based on attractive bonds. If strong repulsive interactions are added to the crystal graph, the situation may occur that energetically a reconstructed face, having a larger surface periodicity, is favoured. An example is the  $(001)$  face of the caesium chloride structure. This crystal face has been modelled using the two-component BCSOS model with repulsive next-nearest-neighbour interactions (Mazzeo *et al.*, 1995). They find a  $c2 \times 2$  reconstructed flat phase for the  $(001)$  face.

In our model graph, this situation corresponds to repulsive  $a$  and  $b$  bonds and SOS bonds  $c$  and  $d$ . The resulting  $c2 \times 2$  reconstruction can be derived from a connected net analysis when the flatness criterion (see §3.1) is suspended. Then, the connected net as depicted in Fig. 9 is a valid connected net. Note that the  $c$  and  $d$  bonds are drawn although the bond energies are similar.

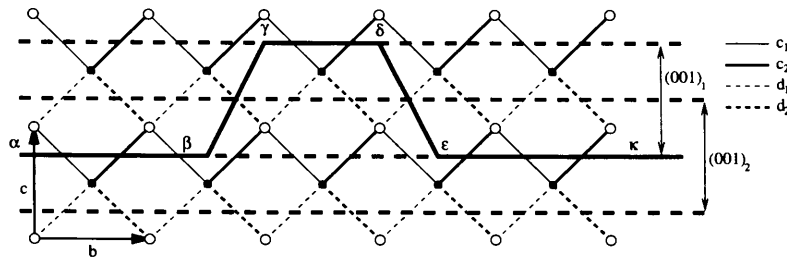


Fig. 7.  $[100]$  projection of the  $(001)$  face of the crystal graph of Fig. 2 with bonds  $c_1$ ,  $c_2$ ,  $d_1$ ,  $d_2$  and  $a = b = 0$ . Steps along  $[100]$  and  $[010]$  are equivalent.

The connected net shown has a symmetry-related connected net translated over  $[100]$ . These two connected nets do not cause symmetry roughening because there is a step energy to go from one connected net to the symmetry-equivalent one. The step energy corresponds in this case to the formation of a domain wall between the two reconstructed surface configurations and implies the formation of a repulsive  $a$  bond.

It is interesting that, depending on the ratio of the bond energies, the crystal face will behave differently when the temperature is increased. This can be seen in the phase diagram for this model in Mazzeo *et al.* (1995). It is shown that, for some specific ratio of bond energies  $\Phi_a/\Phi_b$ , the crystal surface is reconstructed flat at low temperature, rough at higher temperatures and will become disordered flat at very high temperatures. This implies that the crystal face becomes flat at high temperatures instead of rough! Mazzeo *et al.* (1995) refer to this situation as an *inverse roughening* transition.

#### 4. Symmetry of connected nets

##### 4.1. Broken-bond description

A connected-net analysis of a crystal structure often yields a series of connected nets for a single orientation  $(hkl)$  which may also be interpreted as a number of different surface configurations. We will denote a connected net by  $\mathbf{k}_{hkl}^n$ , where the superscript  $n$  labels the different connected nets for the orientation  $(hkl)$  having a normal  $\mathbf{k}_{hkl}$  with  $|\mathbf{k}_{hkl}| = 1/d_{hkl}$ . When a crystal has the lowest possible symmetry  $P1$ , all the connected nets are unique surface configurations but for crystals with higher symmetry connected nets may be related by symmetry.

In general, a symmetry operator  $R_i$  of the space group of the crystal transforms a connected net  $\mathbf{k}$  in itself or in another connected net  $\mathbf{k}'$  with a different orientation. In the discussion of symmetry-related connected nets for a crystal face  $(hkl)$ , we will consider all symmetry elements that conserve the orientation. Then two different situations may occur:  $\mathbf{k}' = \mathbf{k}$  and  $\mathbf{k}' = -\mathbf{k}$ . The latter situation we will call *boundary swapping*. Note that boundary swapping gives rise to a pair of connected nets with opposite surfaces.

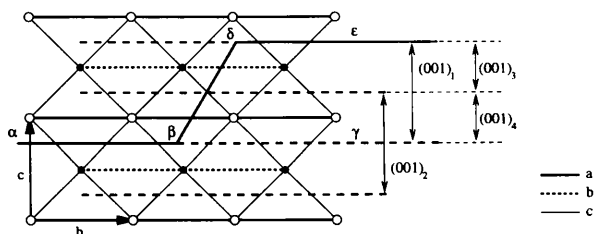


Fig. 8.  $[100]$  projection of the  $(001)$  face of the crystal graph of Fig. 2 with  $d = c$ . Steps along  $[100]$  and  $[010]$  are equivalent.

An example of boundary swapping is shown in Fig. 6. If the space-group symmetry of the graph in Fig. 2 is  $Pmmm$ , the  $(001)_1$  and the  $(001)_2$  connected nets would be related by symmetry elements causing  $\mathbf{k}' = -\mathbf{k}$ . Based on broken bonds, the surface energies of the two connected nets are equal and the step energy for the face is zero. Because of the symmetry, this face will have a roughening temperature of 0 K. This type of roughening we have called symmetry roughening.

It will be shown in a forthcoming paper that a thorough analysis of symmetry relations between connected nets yields the already known BFDH selection rules and, complementary to those, conditions at which symmetry roughening can occur (Meeke *et al.*, 1998).

##### 4.2. Influence of a mother phase

The connected-net analysis is essentially based on bonds between growth units defined in the bulk crystal lattice. Furthermore, the assumption is made that the positions of growth units at an interface are exactly the same as their positions in the bulk crystal. In this section, we consider the situation beyond the broken-bond description, including the effect of a mother phase, relaxation and reconstruction very briefly.

Taking the possibility of surface reconstruction into account, the original HP theory has to be reconsidered somewhat. This was realised by Hartman (1989) and Sun *et al.* (1990) for corundum, hematite and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Including surface reconstruction implies either allowing a larger periodicity at the surface compared with the bulk or relaxing the flatness criterion when one sticks to the periodicity of the bulk lattice.

In the case of surface relaxation, the mesh area  $M_{hkl}$  is not changed with respect to the unrelaxed bulk structure. Then the following symmetry elements will be conserved at the crystal-mother-phase interface:

- all  $n$ -fold rotation axes parallel to  $\mathbf{k}$ ;
- all mirror planes and glide planes parallel to  $\mathbf{k}$  with a glide component perpendicular to  $\mathbf{k}$ .

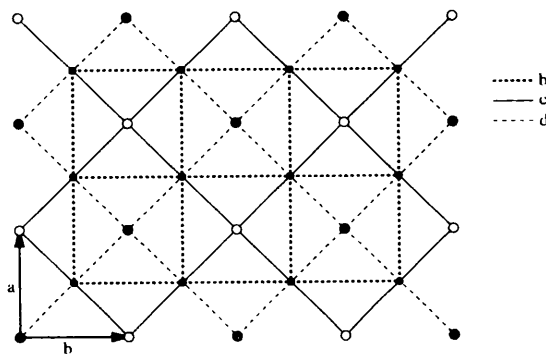


Fig. 9.  $[001]$  projection (top view) of one of the two  $(001)$  connected nets violating the flatness criterion. Black dots:  $B$  growth units; grey dots:  $A$  growth units at  $z = 0$ ; white dots:  $A$  growth units at  $z = 1$ .  $\Phi_c = \Phi_d$ .



In the case of reconstruction, more symmetry elements will be lost, depending on the actual reconstruction. It can be concluded that the symmetry elements causing boundary swapping are lost at the interface. This implies that faces containing symmetry-related connected nets giving rise to boundary swapping and symmetry roughening will formally not roughen at 0 K. In Fig. 6, it can be observed that the two alternative connected nets have either *A* growth units or *B* growth units at the interface. In the broken-bond description, this situation results in equivalent surface energies but it is obvious that these two surfaces will have different surface free energies. However, the free-energy difference might be very small and then the crystal face will become rough even at very low temperatures.

In general, the interaction of a mother phase with the crystal face may either increase or decrease the surface free energy and the step free energy for a crystal face (*hkl*). This is due to adsorbed solvent molecules, the presence of complexes or a preordering effect of the mother phase just at the interface, in any case the effect can be very complex. Nevertheless, we will assume that the effect of a mother phase only influences bond energies as long as there is no reconstruction. Relaxation as argued before nevertheless can destroy some symmetry elements.

Therefore, in general, the effect of a mother phase can change the relevant parameters for crystal growth, namely the attachment energy, the step free energy and consequently the roughening temperature. Calculations of the effect of a solvent on the crystal morphology have been performed by several authors; see for example Berkovitch-Yellin (1985), van der Voort (1991*a,b*) and Liu *et al.* (1995*a*).

## 5. Discussion and conclusion

The present definition of an *F* face originates from the idea to integrate the statistical thermodynamical theories of surface phase transitions and the classical Hartman–Perdok theory for derivation of crystal morphology from the crystal structure. It is very important to bring these disciplines of science together in order to improve the understanding of the behaviour of crystals either in thermodynamic equilibrium with their mother phase or under growth conditions.

Statistical thermodynamical surface models have become more and more applicable to complex crystals and have revealed many surface phases like the normal flat, reconstructed flat, disordered flat (DOF) and rough phases. These phases will influence not only the equilibrium but also the growth morphology of crystals.

These models have to be generalized in order to be applicable to a wider range of experimental crystal structures. In this paper, we have shown that, by deri-

vation and subsequent analysis of all connected nets of a crystal structure, the surface phases found by the more sophisticated statistical thermodynamical models can be identified qualitatively.

Analysis of combinations of connected nets is the key in understanding equilibrium and growth behaviour of more complex crystal faces. In the classical HP theory, the slice energy and attachment energy are the most important parameters for the description of the morphology. In our opinion, both the step free energy and the attachment energy are key parameters for understanding the equilibrium and growth behaviour of crystal faces. We have shown that step energies of a crystal face (*hkl*) can become very small for specific combinations of connected nets even in the case of very high slice energies. In such cases, the roughening temperature of the crystal face can be much lower than expected on the basis of calculated Ising transition temperatures of individual connected nets. Moreover, the growth rate for this type of face will be high even at low driving forces owing to a low two-dimensional nucleation barrier. This is in contrast with the usual assumption that the growth rate depends on the attachment energy only.

For small step free energies in a single direction [*uvw*] of a Kossel-like crystal, it has been shown by Burton *et al.* (1951) that the roughening transition temperature is very low. Consequently, such crystal faces will become rough even at low driving forces. Such an anisotropy can be amplified drastically by pairs of connected nets giving rise to very low step free energies for which the slice energies can still be very high. Crystal faces having a very low step free energy in a single direction [*uvw*] and at the same time high slice energies have been found for triacylglyceride and paraffin crystals (Grimbergen, Hollander *et al.*, 1998; van Hoof *et al.*, 1998).

Equation (11) implies that crystal faces having a step free energy of zero in a single direction [*uvw*] are already rough at 0 K. In this special case of symmetry roughening, the step energy for a crystal face (*hkl*) is zero despite the presence of connected nets containing very strong bonds. The roughening temperature of such faces is 0 K and the growth rate will be very high. An example of symmetry roughening is found for naphthalene and anthracene crystals (Grimbergen, Reedijk, Meekes & Bennema, 1998). A complete overview of symmetry relations between connected nets can be found in Meekes *et al.* (1998).

Note that in the analysis of the connected nets calculated energies are not free energies. The statistical thermodynamical models show that the entropic contribution is essential for exact calculation of the roughening transition temperatures and the presence of different types of surface phases. It is a challenge for the future to develop generally applicable methods for calculation of step free energies and surface free energies of crystal surfaces in contact with a mother phase.

In a forthcoming paper, the growth behaviour of crystal faces containing multiple connected nets will be studied using the connected net analysis and Monte Carlo (MC) simulation techniques (Grimbergen, Bennema & Meekes, 1998). The effect of anisotropy in the growth layer will be studied in detail on the basis of the connected nets. A combination of a connected net analysis and subsequent MC crystal growth simulations offers the possibility of predicting crystal morphology as a function of driving force.

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