The morphology of quasicrystals, incommensurate composite crystals and modulated crystals derived from the broken-bond model

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Abstract

The broken-bond model for the surface free energy of crystals is considered. The consequences are derived for the morphology of periodic crystals, quasicrystals, incommensurately modulated crystals and intergrowth compounds. It is found that low-index facets on periodic crystals and quasicrystals are the result of finding an optimized position along the vector normal to the surface of the surface plane. The same principle explains the normal facets on modulated crystals and intergrowth crystals. The so-called satellite facets are the result of surface pinning of the phase of the modulated wave. On intergrowth compounds, facets may be found that are stabilized by a combination of both mechanisms. It is shown that the most stable facets on intergrowth crystals are the normal facets that are common to the subsystems, independent of the details of the structure.

1. Introduction

It has been known for a long time that the shape of crystalline solids is that of a multifacetted body (Rottman & Wortis, 1984). It is an experimental fact that all facets are perpendicular to a reciprocal-lattice vector (h, k, l) of the crystal. The simplest model to explain the observations is the Bravais–Friedel–Donnay–Harker (BFDH) law (Friedel, 1907; Donnay & Harker, 1937), which states that the morphological importance of a facet is inversely proportional to the length of the reciprocal vector (h, k, l). Only facets with small indices h, k and l are observed.

Theoretically, facetting can be understood from minimizing the total surface free energy of a given amount of crystalline matter. The surface free energy per unit area $\gamma(\hat{\mathbf{n}})$ is a function of the surface normal $\hat{\mathbf{n}}$ and the Wulff construction can be used to determine the equilibrium shape (Fig. 1) (Wulff, 1901). Facetting results from cusps in $\gamma(\hat{\mathbf{n}})$. To a first approximation, $\gamma(\hat{\mathbf{n}})$ can be replaced by the surface energy. Further approximation allows the latter to be computed within the broken-bond model, whereby the surface energy is associated with the energies of the bonds missing at the surface (Kern, 1987). In accordance with experiment, this leads to cusps in $\gamma(\hat{\mathbf{n}})$ for $\hat{\mathbf{n}}$ in the directions of

reciprocal-lattice vectors. The major cusps occur for $\mathbf{n} = (h, k, l)$ when all indices are small.

Aperiodic crystals lack three-dimensional translation symmetry, but their diffraction patterns do have sharp Bragg reflections (van Smaalen, 1995). Indexing of the reflections can still be performed with integers if more than three are used:

$$\mathbf{H}_s = h_1 \mathbf{a}_1^* + \ldots + h_{3+d} \mathbf{a}_{3+d}^*. \tag{1}$$

The $(3 + d)$ reciprocal basis vectors are mutually incommensurate. As for periodic crystals, facetting is the typical morphological appearance of all types of aperiodic crystals. Initially, this observation did not attract much attention, although the classical theories explaining a facetting morphology all depend on the assumption of a translation symmetric structure. It was the observation of facets on incommensurately modulated crystals, which could not be indexed by three small integers of the average lattice, that provoked research on this subject (Janner *et al.*, 1980). Janner and co-workers made the observation that these so-called satellite facets are in fact perpendicular to a reciprocal vector given by $3 + d$ small integers (1), thus generalizing the BFDH law (Janner *et al.*, 1980; Dam *et al.*, 1983; Dam & Janner, 1985; Janner & Dam, 1989). Recently, a broken-bond model explaining the stability of incommensurate facets has been given (van Smaalen, 1993). A superspace approach to a broken-bond model was developed by Bennema and co-workers (Kremers *et al.*, 1995).

Soon after the discovery of quasicrystals, it became apparent that these aperiodic phases also exhibit a facetting morphology (Dubost *et al.*, 1986; Ohashi & Spaepen, 1987; Ho, 1991). Different shapes have been observed, all of them reflecting the noncrystallographic point symmetry. The occurrence of facets on quasicrystals could be explained by the broken-bond model (Ho *et al.*, 1987; Henley & Lipowsky, 1987; Garg & Levine, 1987) and it was proposed that ordered quasicrystals as well as phases with only bond-orientation order (BOO) should exhibit facetting (Ho *et al.*, 1987).

In this paper, the broken-bond model is revisited. Originally, the broken-bond model was developed for crystals with bonds equal to lattice translations or simple

fractions of them (Mackenzie *et al.*, 1962; Mackenzie & Nicholas, 1962; Landau, 1965). A generalization towards the case with lattice periods larger than the bonds was proposed and dismissed by Mackenzie & Nicholas (1962). Here, this generalization is considered again. It is argued that the surface free energy does depend on the position of the surface plane along its normal direction and that it does not depend on its orientation alone. Accordingly, the broken-bond model is reformulated for quasicrystals and modulated structures.

In the second half of the paper, the broken-bond model is formulated for incommensurate composite crystals. The generalization discussed in the first half of the paper appears to be an essential ingredient for the extension of the theory towards this type of aperiodic structure. The reason for these complications is the absence of BOO in composite crystals, as opposed to the presence of BOO in periodic structures, quasicrystals and modulated crystals. Different types of facets on composite crystals are identified and the consequences are derived for the morphological importance of them.

2. The broken-bond model

The energy of the crystal is considered as the sum over a pair potential. For a facet defined by its normal vector of unit length, $\hat{\mathbf{n}}$, the surface energy per unit area, $\gamma(\hat{\mathbf{n}})$, is obtained by adding up the energies of the bonds missing at the surface and dividing the result by the surface area (Kern, 1987).

A bond j is characterized by the vector $\mathbf{A}^j$ between the two atoms defining this bond, the bond length A^j, and the energy J^j assigned to this bond. All bonds with the same $\mathbf{A}^j$ and J^j are denoted as bonds of type μ. For computational reasons, a bond from atom j_1 towards atom j_2 is considered independently from a bond of j_2 towards j_1. It is assumed that the crystal is homogeneous, such that it is meaningful to define the density of bonds

of type μ. For periodic crystals, these concepts are easily interpreted. One particular bond j originating on an atom j_1 is repeated every unit cell and the density of bonds of type μ therefore is $n_\mu = 1/V$. Because the direction of a bond is essential to determine whether the bond is cut by a particular surface, point symmetry is not included in the definition of types of bonds.

Consider a facet given by a direction $\hat{\mathbf{n}}$, which is not parallel to a reciprocal-lattice vector $\mathbf{H} = (h, k, l)$. Then the number of bonds $\overline{N}_\mu$ of type μ actually cut by this surface per unit area is (Mackenzie *et al.*, 1962)

$$\overline{N}_\mu = \begin{cases} n_\mu \, \hat{\mathbf{n}} \cdot \mathbf{A}_\mu & \text{for } \hat{\mathbf{n}} \cdot \mathbf{A}_\mu > 0 \\ 0 & \text{for } \hat{\mathbf{n}} \cdot \mathbf{A}_\mu < 0, \end{cases} \qquad (2)$$

leading to the surface free-energy density

$$\gamma(\hat{\mathbf{n}}) = \sum_\mu J_\mu n_\mu \hat{\mathbf{n}} \cdot \mathbf{A}_\mu \theta(\hat{\mathbf{n}} \cdot \mathbf{A}_\mu), \qquad (3)$$

where the summation is over all bond types μ. The Heavyside step function $\theta(x)$ is defined as $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$. It is thus ensured that only outward-pointing bonds contribute to the summation. Alternatively, the terms can be combined pairwise for bonds from j_1 to j_2 and from j_2 to j_1, resulting in

$$\gamma(\hat{\mathbf{n}}) = \tfrac{1}{2} \sum_\mu J_\mu n_\mu |\hat{\mathbf{n}} \cdot \mathbf{A}_\mu|. \qquad (4)$$

Equation (3) leads to cusps in $\gamma(\hat{\mathbf{n}})$ for $\hat{\mathbf{n}}$ perpendicular to a bond type $\mathbf{A}_\mu$ (Landau, 1965).

The simple argument considers only bonds parallel to lattice vectors. Then, (4) describes cusps in $\gamma(\hat{\mathbf{n}})$ for $\hat{\mathbf{n}}$ perpendicular to a lattice vector, *i.e.* for $\mathbf{n}$ equal to a reciprocal-lattice vector, in accordance with the BFDH law (Landau, 1965). This simple model is realised in only a few structures, like the cubic close-packed (c.c.p.) structure as is found for many metals and noble gases (Mackenzie *et al.*, 1962; Mackenzie & Nicholas, 1962).

Crystals with more than one atom in the unit cell also exhibit facets, and the theory needs to be generalized (Mackenzie & Nicholas, 1962). If the unit cell contains more than a few atoms, the strong bonds will be shorter than the fundamental translations, and facets will develop that avoid cutting these bonds instead of avoiding cutting the 'bond' respresented by the lattice translation. The simple argument based on (4) would lead to facets parallel to the strong bonds. Because bonds are oriented arbitrarily with respect to the lattice translations, these would-be facets are not perpendicular to a reciprocal-lattice vector, contrary to the observations.

The reason for the stability of the facets on periodic crystals with a more complicated structure is the possibility for the surface to become rough on the atomic level. Once an energetically favorable cut through one unit cell has been obtained, this cut can be continued periodically and a low-index facet results. Mathematically, this variety of choices for the actual surface
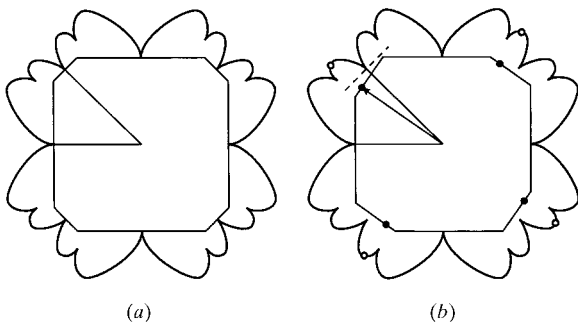

Fig. 1. The Wulff construction for a two-dimensional periodic crystal. The surface free energy in the direction of $\hat{\mathbf{n}}$ is given as the distance to the origin. (*a*) For the classical form of $\gamma(\hat{\mathbf{n}})$, cusps lead to facets on the crystal surface. (*b*) Surface pinning of the phase of the modulation in modulated and intergrowth structures leads to discontinuities in $\gamma(\hat{\mathbf{n}})$ for directions determined by the incommensurate vector $\mathbf{q}$, which are not related to cusps.

structure of a facet of given orientation can be described by the property that lattice planes do not cut through all parts of the unit cell but sample only a discrete equally spaced set of planes. These planes are the collection of Miller planes (Mackenzie & Nicholas, 1962).

For $\hat{\mathbf{n}}$ parallel to a reciprocal-lattice vector, the fraction of the bonds of type μ that is cut by the surface plane is different from (2). Using the fact that the surface unit cell has area $V|\mathbf{n}|$ and that there is one atom per surface unit cell in each Miller plane shows that the number of bonds cut per unit area is either less or more than (2):

$$\overline{N}_\mu = n_\mu \frac{\lfloor \mathbf{H} \cdot \mathbf{A}_\mu \rfloor}{|\mathbf{H}|} \quad \text{or} \quad \overline{N}_\mu = n_\mu \frac{\lfloor \mathbf{H} \cdot \mathbf{A}_\mu \rfloor}{|\mathbf{H}|} + \frac{n_\mu}{|\mathbf{H}|} \quad (5)$$

for $\mathbf{H} \cdot \mathbf{A}_\mu > 0$, and otherwise zero; $\lfloor x \rfloor$ is the largest integer smaller than x. Accordingly, the contribution of the bonds of type μ to the surface free energy can be either one of two values as well, depending on the position δ of the surface along its normal $\hat{\mathbf{n}}$.

The surface free energy becomes dependent on the position of the cutting plane along its normal and the actual surface will correspond to the position leading to a minimum surface free energy. That is, the surface that is realised corresponds to the cutting plane with the optimized value for δ. A schematic example is given in Fig. 2, where the surface may correspond to the weak bonds broken (preferred) or to the strong bonds broken (improbable). For molecular crystals, *e.g.* benzene, the crystal will always contain complete molecules, and the chemical bonds within the benzene molecules will never be broken at a surface. The layered compound NbS_2 will show facets that are the result of a cut through the Van der Waals gap, *i.e.* the surface layer of atoms will be sulfur atoms and never niobium atoms.

Further understanding is obtained from the combination of translation symmetry and strong bonding. If each connected net of strong bonds is localized (*e.g.* the molecular crystal of benzene), it is possible to avoid cutting these bonds for any direction of the facet by simply making the facet rough in the appropriate way on an atomic scale. If an extended chain of strong bonds exists in the crystal, then on the average this chain of bonds is necessarily parallel to a lattice vector (Fig. 2). This is the periodic bond chain (p.b.c.) defined by Hartman & Perdok (Hartman & Perdok, 1955; Hartman, 1987). In the p.b.c. theory, the most stable facets are those containing the maximum number of p.b.c.'s consisting of the strongest bonds. Important facets will contain at least two non-parallel p.b.c.'s. Because a p.b.c. is always on the average parallel to a lattice vector, facets must be parallel to a lattice plane and they are perpendicular to a reciprocal-lattice vector. The p.b.c. theory thus becomes a special case of the generalized broken-bond model. In the latter theory, cutting is avoided of any bond in a p.b.c. through the

choice of the optimal position of the surface plane along $\hat{\mathbf{n}}$.

Taking into account that different atoms (different μ) have different positions but that there is only one surface, the expresssion for the surface free energy becomes (Mackenzie & Nicholas, 1962)

$$\gamma_H(\hat{\mathbf{n}}) = \sum_\mu J_\mu \, n_\mu \, \frac{\lceil \mathbf{H} \cdot \mathbf{A}_\mu + \delta - \delta r_\mu^0 \rceil}{|\mathbf{H}|} - \frac{\lceil \delta - \delta r_\mu^0 \rceil}{|\mathbf{H}|},$$

$$(6)$$

where $\lceil x \rceil$ is the smallest integer larger than x. The position of the cutting plane is defined by $\mathbf{H} \cdot \mathbf{r} = -\delta$ and the different positions are all contained in the interval $0 \le \delta < 1$. δr_μ^0 is the minimum distance between an atom in the crystal and the surface plane $\delta = 0$. It is obvious that (6) reduces to (3) in the limit of large indices, that is for $|\mathbf{H}| \to \infty$.

3. Quasicrystals

A simple model for the structure of quasicrystals is provided by the Penrose tiling (PT). The three-dimensional Penrose tiling (3DPT) is a model for icosahedral quasicrystals, whereas the 2DPT and its generalizations describe structures of quasicrystals with octagonal, decagonal and dodecagonal symmetries. The Penrose tiling consists of two unit cells, which are arranged in a strictly aperiodic way. Important properties are that the edges of the unit cells can be in only a few orientations (*i.e.* BOO exists) and that the tiling is homogeneous in the sense that the density of each type of unit cell is a constant when it is calculated over a sufficiently large
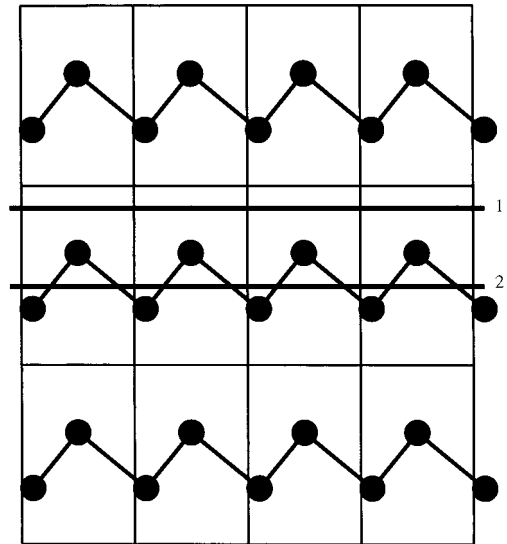

Fig. 2. A periodic bond chain and two choices for the cutting plane defining the surface. Surface plane 1 cuts only weak bonds and will be realised; cutting position 2 is highly unfavorable and will not be realised. Note that the planes have the same orientation.

volume or area. The vertices of the Penrose tiling can be obtained from the superspace description of quasicrystals, with one 'superspace atom' at the origin of the superspace lattice (Janot, 1992).

Based on the above-mentioned properties of the Penrose tiling, the elementary version of the broken-bond model can be generalized immediately [(3) and (4)] (Ho et al., 1987; Henley & Lipowsky, 1987; Garg & Levine, 1987):

$$\gamma_Q(\hat{\mathbf{n}}) = \frac{1}{2} \sum_\mu J_\mu n_\mu |\hat{\mathbf{n}} \cdot \mathbf{A}_\mu|, \tag{7}$$

where n_μ now is the density of edges in the Penrose tiling and $\mathbf{A}_\mu$ represent the edges, which for icosahedral symmetry comprise a star of 12 oriented 'bonds'.

Real quasicrystals have several atoms in the two unit cells of the Penrose tiling or they cannot be described by a Penrose tiling at all. In both cases, their structures can be completely described in superspace, where there are several 'superspace atoms' in the higher-dimensional unit cell. From these descriptions, it can be derived that BOO remains but that bonds may have arbitrary orientation with respect to the higher-dimensional translation periods or edges of the Penrose tiling. From (7), it follows that quasicrystals should develop facets parallel to the strong bonds $\mathbf{A}_\mu$, owing to cusps in the surface free energy. This is not what is observed. Quasicrystals have facets perpendicular to the low-index reciprocal vector $\mathbf{H}_s$ (1), and their orientation is not related directly to the directions of the bonds. A similar type of generalization is required, as was made for periodic crystals (§2).

The generalized form of $\gamma_Q(\hat{\mathbf{n}})$ would require exact counting at what points the surface plane cuts each type of bond. I have not been able to derive the exact formula. However, to show that the stabilization of low-index facets on quasicrystals is the result of optimizing the position of the cutting plane, as it is for periodic crystals, it is sufficient to consider the Penrose tiling. By
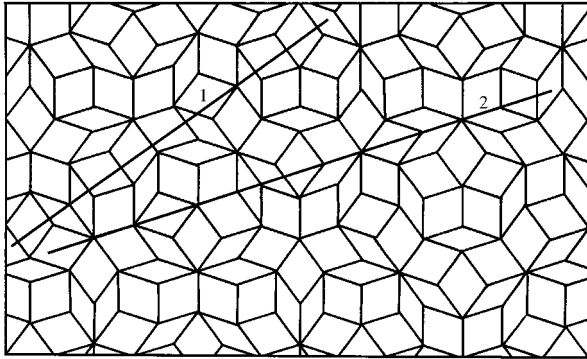

Fig. 3. The two-dimensional Penrose tiling. Both facets with the normal vector along a cell edge (1) and facets with the normal perpendicular to a cell edge (2) are commensurate with the tiling and the surface free energy may be minimized by optimizing the position of the cutting plane.

inspection, it is easily seen that a plane through a worm (or track) traces each of the two unit cells in only a few different positions (Fig. 3, see Garg & Levine, 1987). As in structures that can be described by the decorated Penrose tiling, one type of bond will always have the same position with respect to the different unit cells. It follows that these bonds are cut in a finite number of different ways. Optimization is possible of the position δ of the cutting plane along $\hat{\mathbf{n}}$, in a similar way to that found for periodic crystals. Without proof, it is proposed that the surface free energy of quasicrystals for reciprocal vectors with integer indices [equation (1)] becomes [equation (6)]

$$\gamma_{QH}(\hat{\mathbf{n}}) = \sum_\mu J_\mu n_\mu \frac{\lceil \mathbf{H}_s \cdot \mathbf{A}_\mu + \delta - \delta r_\mu^0 \rceil}{|\mathbf{H}_s|} - \frac{\lceil \delta - \delta r_\mu^0 \rceil}{|\mathbf{H}_s|}, \tag{8}$$

where it has been used that each slice of thickness $|\mathbf{H}_s|^{-1}$ and area $|\mathbf{H}_s|/n_\mu$ contains one bond of type μ. δr_μ^0 is the smallest distance between the cutting plane and an atom of type μ. Equations (7) and (8) represent the same mechanism of the stabilization for facets on quasicrystals as results from (6) and (3) for periodic crystals.

4. Incommensurately modulated structures

Incommensurately modulated crystals have an average structure with translational symmetry. In the average structure, we can enumerate the atoms in the unit cell and the corresponding bond types μ. The real structure corresponds to a periodic variation of the atomic positions, with a period defined by $\mathbf{q} = \mathbf{a}_4^*$ that is incommensurate with the three average translation periods [one-dimensional modulation; equation (1)]. Usually, the modulation is descibed by the fourth coordinate

$$\bar{x}_4^j = \mathbf{q} \cdot (\mathbf{x}_\mu^0 + \mathbf{L}^j) + t, \tag{9}$$

where $\mathbf{L}^j$ are lattice vectors of the average structure and t is the initial phase of the modulation.

Because the atomic positions are modulated, the lengths and the directions of the bonds will also be modulated. In a first approximation, the bond energy can be considered as a function of the bond length only. Instead of one value for the energy of a bond of type μ, the energy will be different for all bonds in the crystal: J_μ becomes the function $J_\mu(\bar{x}_4^j)$. The modulation functions are periodic with period 1 in $\bar{x}_4$, and it follows that $J_\mu(\bar{x}_4)$ is also a periodic function.

The most commonly observed facets on incommensurately modulated crystals are those perpendicular to a reciprocal-lattice vector $\mathbf{H} = (h, k, l)$ of the average structure. Other facets are the so-called incommensurate facets perpendicular to $\mathbf{H}_s$, with at least one of the indices h_k $(k \geq 4)$ nonzero [equation (1)]. It can be shown that a plane $\hat{\mathbf{n}}$ at an irrational angle to the satellite facets cuts the bonds j of type μ at different values of the

phase for different j. That is, the phases $\overline{x}_4^j$ (mod 1) form a dense set in the interval $[0; 1\rangle$. It was argued (van Smaalen, 1993) that for modulated crystals we may define the bonds that are cut at the surface on the basis of the average positions of the atoms and the average bond vectors $\mathbf{A}_\mu$. Then, for a direction irrational to the normal facets as well as irrational to the satellite facets, the surface free energy becomes

$$\gamma_0(\hat{\mathbf{n}}) = \sum_\mu \langle J_\mu \rangle \, n_\mu \, \hat{\mathbf{n}} \cdot \mathbf{A}_\mu \, \theta(\hat{\mathbf{n}} \cdot \mathbf{A}_\mu), \qquad (10)$$

which is the same expression as (3), with the bond energy replaced by its average value

$$\langle J_\mu \rangle = \int_0^1 J_\mu(\overline{x}_4) \, d\overline{x}_4 \qquad (11)$$

The integration is over one period of the periodic function $J_\mu(\overline{x}_4)$.

The normal facets (h, k, l) have irrational orientations with respect to the satellite directions (h, k, l, m) $(m \neq 0)$. The generalization of (6) thus is obtained as

$$\gamma_H(\hat{\mathbf{n}}) = \sum_\mu \langle J_\mu \rangle n_\mu \, \frac{\lceil \mathbf{H} \cdot \mathbf{A}_\mu + \delta - \delta r_\mu^0 \rceil}{|\mathbf{H}|} - \frac{\lceil \delta r_\mu^0 - \delta \rceil}{|\mathbf{H}|}. \qquad (12)$$

It follows that the observation of normal facets on modulated crystals is explained in a way similar to periodic crystals.

The satellite facets (h, k, l, m), with $m \neq 0$, have irrational orientations with respect to the average lattice. It is sufficient to derive the generalization of (3). All bonds j of a given type μ are considered explicitly. Let $\mathbf{A}_\mu^j$ be such a bond. Denote by $\mathbf{r}(j)$ the position of the atom j from which this bond emanates, and let the phase of the modulation wave be $\overline{x}_4^j$ at atom j. From (11), we can derive a modulation contribution to the energy of bond j as $J_{M\mu}^j(\overline{x}_4) = J_\mu^j(\overline{x}_4) - \langle J_\mu \rangle$, for which the average value is zero by definition. The modulation contribution to the surface free energy of an incommensurate facet, γ_M, is then defined by

$$\gamma(\hat{\mathbf{n}}) = \gamma_0(\hat{\mathbf{n}}) + \gamma_M(\hat{\mathbf{n}}). \qquad (13)$$

As before, it is assumed that the surface atoms are defined by the position of the cutting plane and by their average positions $\mathbf{r}_\mu^j = \mathbf{x}_\mu^0 + \mathbf{L}^j$. Let δr_μ^j be the distance of atom j from the surface plane (Fig. 4). It was then derived (van Smaalen, 1993) that the phase of the modulation at atom j can be written as

$$\overline{x}_4^j = -\frac{1}{m}|\mathbf{H}_s|\delta r_\mu^j - \frac{\overline{x}_{\mu 4}^0}{m} - \frac{l^j}{m} + t, \qquad (14)$$

where $\mathbf{H}_s = \mathbf{G} + m\mathbf{q}$ and $\mathbf{G}$ denotes a reciprocal-lattice vector of the average structure; $\overline{x}_{\mu 4}^0 = \mathbf{G} \cdot \mathbf{x}_\mu^0$; and $l^j = \mathbf{G} \cdot \mathbf{L}^j$ is an integer.

To derive the modulation contribution to the surface free energy, a slab below the surface is considered of thickness D. The number of bonds of type μ per unit surface area within this slab is $n_\mu D$ and the total number of these bonds in a large part of the surface of this orientation is N_μ. When j enumerates these bonds, the surface free energy per unit area becomes the average

$$\gamma_M(\hat{\mathbf{n}}) = \sum_\mu \frac{1}{N_\mu} \sum_{j=1}^{N_\mu} J_{M\mu}(\overline{x}_4^j) n_\mu D \, \theta[\hat{\mathbf{n}} \cdot \mathbf{A}_\mu(\overline{x}_4^j) - \delta r_\mu^j]. \qquad (15)$$

The Heavyside step function limits contributions to the summations to those bonds that are actually cut by the surface plane. It is assumed that D is taken sufficiently large as to include every term j corresponding to a bond that can be cut by the surface plane. The factor D/N_μ makes sure that $\gamma_M(\hat{\mathbf{n}})$ becomes independent of D in the limit of large D.

$\gamma_M(\hat{\mathbf{n}})$ depends on j through δr_μ^j and through the integer l^j [equation(14)]. A satellite facet has irrational orientation with respect to the lattice of the average structure and it follows that the set of values δr_μ^j are dense in the interval $[0; D\rangle$ when N_μ goes to infinity. The periodicity of the modulation implies that $\overline{x}_4$ can be taken modulo 1. With $l = l^j \,(\mathrm{mod}\, m)$, only m different values for l occur and it is valid that for each of these values $l = 0, \ldots, m - 1$ the set of values δr_μ^j is dense in the interval $[0; D\rangle$ again. The summation over j can then be replaced by the averages over l and δr^j according to:

$$(1/N_\mu)\sum_{j=1}^{N_\mu} \longrightarrow (1/m) \sum_{l=0}^{m-1} (m^{-1}|\mathbf{H}_s|D)^{-1} \int_0^{(1/m)|\mathbf{H}_s|D} d\tau, \qquad (16)$$

where τ corresponds to $(1/m)|\mathbf{H}_s|\delta r_\mu^j$ according to the substitution

$$\overline{x}_4^j \longrightarrow \overline{x}_{\mu 4} = -\tau - l/m - \overline{x}_{\mu 4}^0/m + t. \qquad (17)$$
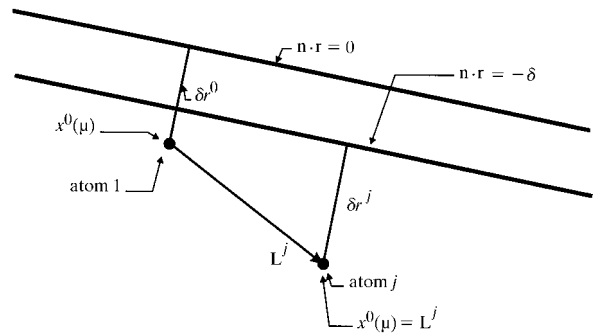

Fig. 4. The plane defining the crystal surface. δr^0 is defined as the distance of atom $j = 1$ to the plane $\delta = 0$; δr^j is defined as the distance of atom j to the plane δ. $\mathbf{r}_{p\mu}^j = \mathbf{r}_\mu^j + \delta r_\mu^j$ is the projected position of atom j onto the cutting plane.

In the limit of large D, this leads to the following expression for the contribution of the modulation to the surface free energy:

$$\gamma_M(\hat{\mathbf{n}}) = \sum_\mu \sum_{l=0}^{m-1} (1/|\mathbf{H}_s|) \int_0^\infty n_\mu J_{M\mu}[|\mathbf{A}_\mu(-\tau - l/m$$
$$- \bar{x}_{\mu 4}^0/m + t)|] \theta[(1/m)\mathbf{H}_s \cdot \mathbf{A}_\mu(-\tau - l/m$$
$$- \bar{x}_{\mu 4}^0/m + t) - \tau] \mathrm{d}\tau. \qquad (18)$$

If $\mathbf{A}_\mu$ within the step function is replaced by its average value, the integral reduces to

$$\gamma_M(\hat{\mathbf{n}}) = \sum_\mu \sum_{l=0}^{m-1} (1/|\mathbf{H}_s|) \int_0^{\tau^{\max}} n_\mu J_{M\mu}[|\mathbf{A}_\mu(-\tau - l/m$$
$$- \bar{x}_{\mu 4}^0/m + t)|] (1/m)|\mathbf{H}_s \cdot \mathbf{A}_\mu| \, \mathrm{d}\tau \qquad (19)$$

with $\tau^{\max} = (1/m|)\mathbf{H}_s \cdot \mathbf{A}_\mu| \, (\mathrm{mod}\, m)$. This is the generalization of the corresponding equation in van Smaalen (1993).

It follows that the surface free energy per unit area for orientations corresponding to a satellite facet depends on $\mathbf{H}_s$ and on m independently. It was shown previously that γ_M goes to zero faster than $1/|\mathbf{H}_s|$ and faster than $1/|m|$ when either $|\mathbf{H}_s|$ or $|m|$ or both go to infinity (van Smaalen, 1993). When all indices are small, γ_M may be nonzero. By optimizing the phase of the modulation t, the modulation contribution to the surface free energy may always be made negative, and a stabilization of low-index satellite facets results as compared to the irrational facets [equation (10)].

The stabilization of the normal facets on modulated crystals has the same origin as for periodic crystals. It is due to the possibility of avoiding cutting strong bonds for facets of low-index lattice directions. The stabilization of satellite facets is due to the selection of phases of the modulation. Through pinning of the phase of the modulation wave at the surface, only those bonds are cut that have an energy smaller than average, while bonds stronger than average are retained. Whether satellite facets occur in the morphology appears to be a matter of chance. It depends on the details of the structure. They can be expected when a particular satellite facet with a large negative γ_M, the strong bonds and the average lattice of the structure are in a favorable relative orientation.

A special treatment is required for normal facets that are perpendicular to a vector $\mathbf{H}_s = \mathbf{G} + m\mathbf{q}$ at the same time. Here, $\mathbf{G}$ denotes a reciprocal-lattice vector of the average structure and $m \neq 0$. For structures with a one-dimensional modulation, this situation can occur for one facet only, provided that the modulation wavevector has exactly one irrational component. Otherwise, such facets cannot occur. The effect is that such a facet is stabilized, both by the selection of the appropriate cutting plane $\gamma_H(\hat{\mathbf{n}})$ and by pinning of the phase of the modulation wave at the surface [$\gamma_M(\hat{\mathbf{n}})$]. The expression for the surface free energy density of such facets is derived in Appendix A.†

5. Incommensurate intergrowth compounds

The atoms in incommensurate intergrowth compounds can be assigned exclusively to one or another of the finite number of subsystems (van Smaalen, 1995). (Presently known compounds have two or three subsystems.) Each subsystem has the structure of an incommensurately modulated structure, with an average translation symmetry and a modulation. Subsystems are mutually incommensurate and periods of the modulations in one subsystem correspond to translation periods of the average structures of the other subsystems. The compound does not have average three-dimensional translation symmetry but a basic structure can be defined as the intergrowth of translational symmetric subsystems, where each subsystem is given its average structure.

Each Bragg reflection (1) can be assigned to one of a few different classes. The first group of reflections contains the reflections that are main reflections of two subsystems at the same time. Usually they comprise a two-dimensional reciprocal lattice. The second group of reflections is those that are main reflections of one subsystem and satellite reflections of varying orders of the other subsystems. There is one group of this type for each subsystem. Finally, there are the reflections that are satellite reflections for all subsystems. If there are more than two subsystems, a more refined classification is possible by, for example, considering the group of reflections that are main reflections for three subsystems (a one-dimensional reciprocal lattice).

Orientations for possible facets on the crystal can be classified in the same way as Bragg reflections. Normal facets have indices corresponding to Bragg reflections common to all subsystems. The second type of facet has indices corresponding to the second group of Bragg reflections, *i.e.* they are normal facets for one subsystem but they are satellite facets for the other subsystems. The true satellite facets have indices corresponding to the last group of reflections, *i.e.* they are satellite facets for all subsystems. Finally, there are the irrational orientations, which are orientations that cannot be indexed with small indices on the basis of (1).

Two classes of bonds have to be considered explicitly. First, a bond between two atoms within one subsystem can be treated in a way similar to the treatment of bonds in an incommensurately modulated structure, and contributions to the surface free energy can be obtained from (10), (12) and (18). The contributions of the different subsystems need to be added to obtain the contributions of all broken bonds to the surface free energy.

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† Appendix A has been deposited and is available from the IUCr electronic archives (Reference: SE0245). Services for accessing these data are described at the back of the journal.

The second type of bond is between an atom of one subsystem and an atom of another subsystem. Interatomic distances for this type of coordination have already been considered extensively (van Smaalen, 1995). It was found that, given the values of $\mathbf{L}^j$ and x_μ^0 for the two atoms, their distance depends on the incommensurate phase and it varies continuously between a minimum value and infinity. Furthermore, the direction of the bond was found to depend continuously on the phase of the modulation wave. The expressions for the surface free energy of a modulated structure cannot be used for this type of bond.

The periodicities and atomic coordinates of each of the subsystems in an intergrowth compound can be specified in exactly the same way as for modulated crystals. To distinguish the different subsystems, all symbols get the subscript or superscript ν ($\nu = 1, 2, \ldots$ for the first subsystem, the second subsystem, $\ldots$). The relation between the structure of the crystal and the structures of the subsystems is contained in the W^ν matrices. Each subsystem is characterized by a $(3 + d) \times (3 + d)$ integer matrix, defined by ($i = 1, 2, 3$; $l = 1, \ldots, d$)

$$\mathbf{a}_{\nu i}^* = \sum_{k=1}^{3+d} W_{ik}^\nu \mathbf{a}_k^*$$
$$\mathbf{q}^{\nu l} = \sum_{k=1}^{3+d} W_{3+l,k}^\nu \mathbf{a}_k^*. \qquad (20)$$

$\Lambda_\nu^* = \{\mathbf{a}_{\nu 1}^*, \mathbf{a}_{\nu 2}^*, \mathbf{a}_{\nu 3}^*\}$ is the reciprocal lattice of the average structure of subsystem ν and $\mathbf{q}^{\nu l}$ are the modulation wave vectors. The corresponding direct lattice is denoted by Λ_ν.

The coordinates and the modulation functions of the atom j of type μ of subsystem ν with respect to the lattice Λ_ν are given by

$$x_{\nu i}^j(\mu) = \overline{x}_{\nu i}^j(\mu) + u_{\nu i}^\mu[\overline{x}_{\nu 4}^j(\mu), \ldots, \overline{x}_{\nu,3+d}^j(\mu)] \qquad (21)$$

$$\overline{x}_{\nu i}^j(\mu) = L_i^j + x_i^0(\mu) - \sum_{k=1}^d W_{i,3+k}^\nu t_k \qquad (22)$$

$$\overline{x}_{\nu,3+l}^j(\mu) = \mathbf{q}^{\nu l} \cdot \overline{\mathbf{x}}_\nu^j(\mu) + \sum_{k=1}^d W_{3+l,3+k}^\nu t_k \qquad (23)$$

for $i = 1, 2, 3$ and $l = 1, \ldots, d$. The parameters t_k are the initial phases along the d additional dimensions. It is noted that for modulated structures (with only one subsystem) $\sum_{k=1}^d W_{i,3+k}^\nu t_k$ is equal to zero. In composite crystals, the coordinates necessarily become dependent on t for all but one of the subsystems.

It immediately follows that the distance between a pair of atoms of different subsystems will grow indefinitely for $t \to \pm\infty$ and that periodicity in $\overline{x}_{\nu,4}$ is absent, contrary to what was found for the distances in modulated structures. Periodicity can be restored, if we consider the full coordination sphere of a given atom. That is, between one atom of subsystem ν [with given $\mathbf{L}^j$

and $\mathbf{x}^0(\mu)$] and all atoms of subsystem ν' (with varying $j' \in \nu'$) the collection of distances is periodic in each of the phases $\overline{x}_{\nu,3+l}$. Because $\mathbf{q}^{\nu l}$ and $\mathbf{q}^{\nu' l}$ represent different periodicities, contributions to the surface free energy have to be considered separately for bonds emanating from an atom of subsystem ν and for bonds emanating from an atom of subsystem ν'.

5.1. Broken bonds between subsystems

Consider two subsystems ν and ν', and consider the contribution $\gamma^{\nu\nu'}(\hat{\mathbf{n}})$ to the surface free energy owing to missing bonds emanating from atoms of subsystem ν and ending at an atom of subsystem ν'. Let k represent an atom of type μ' of subsystem ν'. Let j enumerate the atoms of type μ of subsystem ν that are below the surface plane, *i.e.* those atoms that are part of the crystal. A bond of type μ is defined as a bond between an atom of type μ in subsystem ν and an atom of type μ' in subsystem ν'. In this way, one type of bond comprises bonds with lengths extending from a minimum value up to infinity. Following (15), the contribution $\gamma^{\nu\nu'}(\hat{\mathbf{n}})$ to the surface free energy is

$$\gamma^{\nu\nu'}(\hat{\mathbf{n}}) = \sum_\mu (1/N_\mu) \sum_{j=1}^{N_\mu} \sum_{k=1}^\infty J_\mu^{\nu\nu'}[|\mathbf{A}_\mu^{jk}(\overline{x}_{\nu 4}^j)|] n_\mu D$$
$$\times \theta[\hat{\mathbf{n}} \cdot \mathbf{A}_\mu^{jk}(\overline{x}_{\nu 4}^j) - \delta r_\mu^j]. \qquad (24)$$

δr_μ^j is the distance between atom j of type μ of subsystem ν and the surface plane; $\mathbf{A}_\mu^{jk}(\overline{x}_{\nu 4}^j)$ is the vector from atom j towards atom k.

To be able to calculate $\mathbf{A}_\mu^{jk}(\overline{x}_{\nu 4}^j)$, the coordinates of the atoms j and k need to be brought onto common axes. The transformation of coordinates from the reference system Λ_ν towards the common reference system corresponding to (1) is given by (van Smaalen, 1991, 1995)

$$Q^\nu = (Z_3^\nu + Z_d^\nu \sigma)^{-1} \qquad (25)$$

with Z_3^ν being the left upper 3×3 part of W^ν and Z_d^ν the right upper $3 \times d$ part. σ is the $d \times 3$ matrix of coordinates of the modulation wave vectors.

The vector characterizing the bond between atom j of subsystem ν and atom k of subsystem ν' becomes [equation (21)]

$$\mathbf{A}_\mu^{jk}(\overline{x}_{\nu 4}^j) = Q^{\nu'} \mathbf{x}_{\nu'}^k(\mu') - Q^\nu \mathbf{x}_\nu^j(\mu). \qquad (26)$$

Equation (26) still depends on $\overline{x}_{\nu 4}^j$ and on $\overline{x}_{\nu' 4}^k$ [equation (21)]. If all k values are allowed, the environment of atom j is equal to the environment of atom $j = 1$ when the latter is taken at the appropriate phase. Define atom $j = 1$ by $\mathbf{L}^j = 0$. Write $t = t^0 + \delta t$, then the required phase shift is (van Smaalen, 1995) (Fig. 4)

$$\delta t^j = (V_d^\nu - \sigma^\nu Z_d^\nu)^{-1} \sigma^\nu \mathbf{L}_\nu^j, \qquad (27)$$

where V_d^ν is the right-lower $d \times d$ part of W^ν. Substitution of this value into (21) and subsequent substitution into (26) gives

$$
\begin{aligned}
\mathbf{A}_\mu^{jk}(\overline{x}_{v4}^j) &= \mathbf{A}_\mu^k(\delta t^j) \\
&= Q^{v'}\mathbf{x}_{v'}^0(\mu') + Q^{v'}\mathbf{L}^k - Q^{v'}Z_d^{v'}(t^0 + \delta t^j) \\
&\quad + Q^{v'}\mathbf{u}_{v'}^{\mu'}[\mathbf{q}^{v'} \cdot \mathbf{x}_{v'}^0(\mu') + \mathbf{q}^{v'} \cdot \mathbf{L}^k(\mu') \\
&\quad + (V_d^{v'} - \mathbf{q}^{v'}Z_d^{v'})(t^0 + \delta t^j)] - Q^v\mathbf{x}_v^0(\mu) \\
&\quad + Q^v Z_d^v(t^0 + \delta t^j) - Q^v\mathbf{u}_v^{\mu}[\mathbf{q}^v \cdot \mathbf{x}_v^0(\mu) \\
&\quad + (V_d^v - \mathbf{q}^v Z_d^v)(t^0 + \delta t^j)].
\end{aligned} \tag{28}
$$

All of the j dependence of $\mathbf{A}_\mu^{jk}(\overline{x}_{v4}^j)$ and thus of $\gamma^{vv'}(\hat{\mathbf{n}})$ has been moved to the parameter δt^j. Dependent on the orientation of the facet, different combinations of values of δr_v^j and $\overline{x}_{v4}^j$ will be found for the broken bonds at the surface.

5.1.1. *Irrational orientations*. First, the facets are considered with irrational orientations $\hat{\mathbf{n}}$. These orientations are incommensurate with all subsystem lattices v, as well as with the modulations. It follows that, within a slab of thickness D below the surface, the values δr_μ^j densely fill the interval $[0; D\rangle$. For each infinitesimal range of values $[\delta r_\mu, \delta r_\mu + d r_\mu\rangle$, the phases $\overline{x}_{v4}^j(t) \,(\mathrm{mod}\, \tau_v^{\mathrm{per}})$ densely fill the interval $[0; \tau_v^{\mathrm{per}}\rangle$, where τ_v^{per} is the periodicity of the coordination of an atom of subsystem v in the phase parameter t, and thus it is the periodicity of $\gamma^{vv'}(\hat{\mathbf{n}})$ [equation (21)]. The summation over the individual atoms j can then be replaced by a double average, according to

$$
\frac{1}{N_\mu}\sum_{j=1}^{N_\mu} \longrightarrow \frac{1}{|\mathbf{n}|D}\int_0^{|\mathbf{n}|D} dx \,\frac{1}{\tau_v^{\mathrm{per}}}\int_0^{\tau_v^{\mathrm{per}}} d\tau. \tag{29}
$$

$|\mathbf{n}|\delta r_v^j$ is to be replaced by x, and δt^j in (28) is to be replaced by τ.

With these substitutions, and in the limit of $D \to \infty$, the contribution to the surface free energy becomes

$$
\begin{aligned}
\gamma_0^{vv'}(\hat{\mathbf{n}}) &= \sum_\mu \frac{n_\mu}{|\mathbf{n}|}\int_0^\infty dx \,\frac{1}{\tau_v^{\mathrm{per}}}\int_0^{\tau_v^{\mathrm{per}}} d\tau \\
&\quad \times \sum_{k \in v'} J_\mu^{vv'}[|\mathbf{A}_\mu^k(\tau)|]\,\theta[\mathbf{n} \cdot \mathbf{A}_\mu^k(\tau) - x].
\end{aligned} \tag{30}
$$

Owing to the dependence of the step function on the phase of the modulation through the dependence of $\mathbf{A}_\mu^k(\tau)$ on τ, it is not possible to obtain a simplified expression like (10) by integrating over x.

5.1.2. *Normal facets*. Facets that are normal facets for subsystem v are commensurate with the subsystem lattice Λ_v. Consequently, δr_μ^j assumes only a finite number of values within a slab of thickness D below the surface plane. The position of the cutting plane δ is defined by $\mathbf{H} \cdot \mathbf{r} = -\delta$, where $\mathbf{H} \in \Lambda_v^*$. All different planes are obtained for $\delta \in [0; 1\rangle$. Define δr_μ^0 as the minimum of the distances between an atom of subsystem v and the surface plane $\delta = 0$. Because each net plane $\mathbf{H}$ of subsystem v contains atoms j, the range of values for δr_μ^0 is $[0; |\mathbf{H}|^{-1}\rangle$. Then the possible values for

the distance between an atom of subsystem v and the surface plane δ are given by

$$
|\mathbf{H}|\delta r_\mu^j = l + |\mathbf{H}|\delta r_\mu^0 - \delta \tag{31}
$$

with $l = 0, 1, 2, \ldots$. The value for $l = 0$ is only included when $|\mathbf{H}|\delta r_\mu^0 - \delta > 0$. The maximum value of l is determined by D.

The facets do have an irrational orientation with respect to the modulation of the first subsystem. Following the discussion in §4, it can be derived that, for each of the different values of δr_μ^j, the phase $\overline{x}_{v4}^j(t)\,(\mathrm{mod}\,\tau_v^{\mathrm{per}})$ is dense in the interval $[0; \tau_v^{\mathrm{per}}\rangle$. Then, the summation over j can be replaced by a summation over l and an integration over δt, according to

$$
\frac{1}{N_\mu}\sum_{j=1}^{N_\mu} \longrightarrow \frac{1}{|\mathbf{H}|D}\sum_{l=0}^{|\mathbf{H}|D}\frac{1}{\tau_v^{\mathrm{per}}}\int_0^{\tau_v^{\mathrm{per}}} d\tau\, \theta(l + |\mathbf{H}|\delta r_\mu^0 - \delta). \tag{32}
$$

In the expression for the free energy, $|\mathbf{H}|\delta r_v^j$ is to be replaced according to (31), and δt^j in (28) is to be replaced by τ. The step function makes sure that the term $l = 0$ is only included for $|\mathbf{H}|\delta r_\mu^0 - \delta > 0$. Substitution into (24) gives

$$
\begin{aligned}
\gamma_H^{vv'}(\hat{\mathbf{n}}) &= \sum_\mu \frac{n_\mu}{|\mathbf{H}|}\sum_{l=0}^\infty \frac{1}{t_v^{\mathrm{per}}}\int_0^{t_v^{\mathrm{per}}}\sum_{k \in v'} J_\mu^{vv'}[|\mathbf{A}_\mu^k(\tau)|] \\
&\quad \times \theta[\mathbf{H} \cdot \mathbf{A}_\mu^k(\tau) + \delta - |\mathbf{H}|\delta r_\mu^0 - l] \\
&\quad \times \theta(l + |\mathbf{H}|\delta r_\mu^0 - \delta)\, d\tau.
\end{aligned} \tag{33}
$$

The second step function determines whether or not the term $l = 0$ is included. The first step function shows that all terms beyond a maximum value of l are zero. The precise number of terms contributing to the summation over l depends on the values of $\mathbf{H} \cdot \mathbf{A}_\mu^k(\tau)$, δr_μ^0 and δ. In particular, it depends on the position of the cutting plane δ.

An analysis of the summation over l similar to that in Mackenzie & Nicholas (1962) leads to the expression for the contribution to the surface free energy:

$$
\begin{aligned}
\gamma_H^{vv'}(\hat{\mathbf{n}}) &= \sum_\mu \frac{n_\mu}{|\mathbf{H}|}\frac{1}{t_v^{\mathrm{per}}}\int_0^{t_v^{\mathrm{per}}}\sum_{k \in v'} J_\mu^{vv'}[|\mathbf{A}_\mu^k(\tau)|] \\
&\quad \times [\lceil\mathbf{H} \cdot \mathbf{A}_\mu^k(\tau) + \delta - |\mathbf{H}|\delta r_\mu^0\rceil \\
&\quad - \lceil\delta - |\mathbf{H}|\delta r_\mu^0\rceil]\, d\tau.
\end{aligned} \tag{34}
$$

[Compare (12) and (6).] For normal facets that are satellite facets at the same time, an additional stabilization due to the modulation is possible. The derivation of the corresponding form of the surface free energy density is given in Appendix B.†

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† Appendix B has been deposited and is available from the IUCr electronic archives (Reference: SE0245). Services for accessing these data are described at the back of the journal.

5.1.3. *Satellite facets*. Satellite facets of subsystem ν have irrational orientations with respect to the subsystem lattice Λ_ν. It immediately follows that the values of δr_μ^j densely fill the interval $[0; D\rangle$. Because these facets are commensurate with the modulation periodicities of subsystem ν, the possible phases of the modulation are restricted to a discrete number of values. A special feature of this type of facet is that the values of δr_μ^j and δt^j are correlated. In a derivation similar to that for modulated structures, it is found that

$$\delta t_\nu^j = -\frac{|\mathbf{H}_s|}{m_\nu}(\delta r_\mu^j - \delta r_\mu^1) - \frac{l^j}{m_\mu} \quad (35)$$

for a satellite facet defined by $\mathbf{H}_s \cdot \mathbf{r} = 0$; $\mathbf{H}_s = \mathbf{G}_\nu + m_\nu \mathbf{q}$ and $\mathbf{G}_\nu$ denotes a reciprocal-lattice vector of Λ_ν^*; $l^j = -\mathbf{G} \cdot \mathbf{L}^j$ is an integer and $\mathbf{L}^1$ is chosen to be zero. δt is obtained by applying the transformation $(V_d^\nu - \sigma^\nu Z_d^\nu)^{-1}$ to δt_ν [equation (27)].

The periodicity of the coordination of an atom of subsystem ν is 1 in δt_ν. This implies that the different values to be considered for l^j are $l = 0, \ldots, m_\nu - 1$. For each $l = l^j \pmod{m_\nu}$, the set of values δr_μ^j is dense in the $[0; D\rangle$ again, and the summation over j can be replaced by an average over δt according to

$$\frac{1}{N_\mu}\sum_{j=1}^{N_\mu} \longrightarrow \frac{1}{m_\nu}\sum_{l=0}^{m_\nu-1}\frac{1}{m_\nu^{-1}|\mathbf{H}_s|D}\int_0^{(1/m_\nu)|\mathbf{H}_s|D} \mathrm{d}\tau, \quad (36)$$

where τ replaces $(1/m_\nu)|\mathbf{H}_s|\delta r_\mu^j$ and δt^j is replaced according to

$$\delta t^j = (V_d^\nu - \sigma^\nu Z_d^\nu)^{-1}(-\tau - l/m_\nu). \quad (37)$$

In the limit of large D, this leads to the following expression for the contribution of the modulation to the surface free energy:

$$\gamma_M^{\nu\nu'}(\hat{\mathbf{n}}) = \sum_\mu \sum_{l=0}^{m-1} \frac{n_\mu}{|\mathbf{H}_s|}\int_0^\infty \sum_{k=1}^\infty J_\mu^{\nu\nu'}\left\{\left|\mathbf{A}_\mu^k\left[(V_d^\nu - \sigma^\nu Z_d^\nu)^{-1}\right.\right.\right.$$
$$\left.\left.\times\left(-\tau - \frac{l}{m_\nu}\right)\right]\right|\right\}\theta\left\{\frac{1}{m_\nu}\mathbf{H}_s \cdot \mathbf{A}_\mu^k\right.$$
$$\left.\times\left[(V_d^\nu - \sigma^\nu Z_d^\nu)^{-1}\left(-\tau - \frac{l}{m_\nu}\right)\right] - \tau\right\}\mathrm{d}\tau. \quad (38)$$

[Compare with (18).]

5.2. *The surface free energy*

The surface free energy of oriented facets on composite crystals is obtained by adding together the appropriate terms from §§5.1.1–5.1.3, combined with the contributions from broken intra-subsystem bonds [equations (10)–(18)]. Because n_μ represents the actual density of bonds of type μ in the crystal, no additional scaling is required.

For irrational orientations, the surface free energy of an incommensurate composite crystal per unit area becomes

$$\gamma_0(\hat{\mathbf{n}}) = \sum_\nu \gamma_0^\nu(\hat{\mathbf{n}}) + \sum_\nu \sum_{\nu'} \gamma_0^{\nu\nu'}(\hat{\mathbf{n}}), \quad (39)$$

where $\gamma_0(\hat{\mathbf{n}})$ from (10) has been given the superscript ν to indicate the subsystem to which it applies, and where the double sum of contributions (30) excludes the diagonal terms $\nu' = \nu$. The summations run over all subsystems.

The surface free energy for other orientations is obtained in a similar way. As an example, consider an intergrowth compound with two subsystems that have the reciprocal-lattice plane $(\mathbf{a}_1^*, \mathbf{a}_2^*)$ in common. The first group of facets consists of normal facets for both subsystems, with possible indices $(h, k, 0, 0)$. The expression for the surface free energy is

$$\gamma_H(\hat{\mathbf{n}}) = \sum_{\nu=1}^2 \gamma_H^\nu(\hat{\mathbf{n}}) + \sum_{\nu=1}^2 \gamma_H^{\nu\nu'}(\hat{\mathbf{n}}), \quad (40)$$

where ν' is the complement of ν and $\gamma_H^\nu(\hat{\mathbf{n}})$ and $\gamma_H^{\nu\nu'}(\hat{\mathbf{n}})$ are given in (12) and (34), respectively. If the facet corresponds to a direction with collinear subsystem reciprocal vectors, $\gamma_H^{\nu\nu'}(\hat{\mathbf{n}})$ needs to be replaced by $\gamma_{MH}^{\nu\nu'}(\hat{\mathbf{n}})$ (Appendix B†).

Facets $(h_1, h_2, h_3, 0)$ are normal facets for subsystem 1, but they are satellite facets for subsystem 2 (with $m_2 = h_3 \neq 0$). The surface free energy follows from (6), (18), (34) and (38), resulting in

$$\gamma(\hat{\mathbf{n}}) = \gamma_H^1(\hat{\mathbf{n}}) + \gamma_0^2(\hat{\mathbf{n}}) + \gamma_M^2(\hat{\mathbf{n}}) + \gamma_H^{1,2}(\hat{\mathbf{n}}) + \gamma_M^{2,1}(\hat{\mathbf{n}}). \quad (41)$$

A similar expression is obtained for facets $(h_1, h_2, 0, h_4)$ by interchanging the superscripts $\nu = 1$ and $\nu = 2$.

The true satellite facets (h_1, h_2, h_3, h_4) have both h_3 and h_4 different from zero. The surface free energy follows from (18) and (38):

$$\gamma(\hat{\mathbf{n}}) = \sum_{\nu=1}^2 [\gamma_0^\nu(\hat{\mathbf{n}}) + \gamma_M^\nu(\hat{\mathbf{n}})] + \sum_{\nu=1}^2 \gamma_M^{\nu\nu'}(\hat{\mathbf{n}}), \quad (42)$$

where again the value of ν' is implied by the value of ν.

This analysis shows that the surface free energy per unit area in irrational directions essentially is given by the average over all values of the incommensurate parameter [equation (39)]. The same is true for facets that are normal facets for all subsystems, but then the position of the cutting plane (δ) can be optimized. The mechanism of stabilization of normal facets thus is the same as for periodic crystals. These are the periodic directions that allow the cutting of strong bonds to be avoided. Facets that are normal facets for one subsystem but satellite facets for the other subsystems allow for

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optimization of the position of the cutting plane (δ) as well as for optimization of the value of the incommensurate parameter (t^0) [equation (41)]. An important parameter for the stabilization of these facets is the relative strength of the bonds within subsystems and the bonds between subsystems, as well as the variation in bond strength implied by the modulation. Finally, for true satellite facets, only the value of the incommensurate phase can be optimized [equation(42)].

6. Discussion

The dependence on the orientation has been derived for the surface free-energy density for the various types of aperiodic crystal. For all types of aperiodic crystal as well as for periodic crystals, a major effect determining the stability of facets was found to be the possibility of finding an optimum cutting position of the surface plane for orientations corresponding to facets with small indices, thus avoiding strong bonds to be cut.

For incommensurately modulated structures and composite crystals, a second mechanism of stabilization of low-index facets corresponds to pinning of the phase of the modulation at the surface. This mechanism of stabilization is responsible for the occurrence of satellite facets. Furthermore, it may contribute to the stabilization of the normal facets, in particular in the case of incommensurate intergrowth compounds. In the following, we will discuss some consequences for the equilibrium morphology of this formulation of the surface free-energy density.

6.1. Periodic crystals and quasicrystals

The classical formulation of the broken-bond model employs (3) or (4) to describe the orientation dependence of the surface energy (*e.g.* Kern, 1987; Mackenzie & Nicholas, 1962; Herring, 1951; Bennema, 1973). The correct orientation of the facets is only obtained if the vectors $\mathbf{A}_\mu$ are taken equal to lattice vectors instead of equal to the chemical bonds. It is argued here that the true origin for the stability of low-index facets lies in the fact that the surface energy of these facets depends on the position of the cutting plane along its normal vector and that an optimized position can be determined for this plane (6). According to this model, the correct morphology is obtained also for crystals where bonds have arbitrary orientations with respect to the lattice (§2).

For quasicrystals, the same mechanism of stabilization is valid as for periodic crystals. Again, the previous treatments of the broken-bond model for quasicrystals only included models with special directions and special lengths of the 'bonds', and it was assumed that (7) would apply (Ho, 1991; Ho *et al.*, 1987; Henley & Lipowsky, 1987; Garg & Levine, 1987; Lipowsky & Henley, 1988; Ingersent & Steinhardt, 1988, 1989). Using bonds

between the cells of the Penrose tiling, the great rhombicosidodecahedron was derived to be the shape for icosahedral quasicrystals. Observations have shown that the morphology of icosahedral quasicrystals is a pentagonal dodecahedron [for *i*-AlCuFe (Ohashi & Spaepen, 1987)], a rhombic triacontahedron [for *i*-AlCuLi (Dubost *et al.*, 1986)], an icosidodecahedron or a rhombic icosidodecahedron (Beeli & Nissen, 1993; Tamura *et al.*, 1996). These shapes include only facets perpendicular to reciprocal vectors describing the strong Bragg reflections of quasicrystals and they are not necessarily correlated with the directions of the bonds. Again, the optimization of the position of the cutting plane along its normal provides the mechanism responsible for the stabilization of the observed facets.

The structures of the surfaces of quasicrystals were studied by various techniques, including scanning tunneling microscopy (Schaub *et al.*, 1994; Ebert *et al.*, 1998), X-ray photoelectron spectroscopy and low-energy electron diffraction (Shen *et al.*, 1997). These studies give support for selective cuts being responsible for the stabilization of low-index facets. In particular, selective cuts have been observed on the fivefold surface of an Al–Pd–Mn icosahedral quasicrystal (Gierer *et al.*, 1997). The LEED patterns of this facet could be fitted only when a selection of all possible surfaces was included in the calculation. The structure of icosahedral AlPdMn in the fivefold direction can be described as a sequence of layers with small spacings (presumably the stronger bonds) and larger spacings (presumably the weaker bonds). The different terminations share the property that the surface is formed by cutting the larger spacing (the weaker bonds) (Gierer *et al.*, 1997) in accordance with the present theory.

Recently, it has been proposed that the structure of quasicrystals can be considered an aperiodic arrangement of overlapping clusters (Burkov, 1991; Janot, 1997; Steinhardt & Jeong, 1996). The chemical bonds between atoms have arbitrary orientations with respect to the quasi-lattice, but the center of the clusters might form a simple Penrose tiling. Consequently, the 'bonds' between clusters do have a definite orientation with respect to the quasi-lattice. Assuming the crystal to comprise complete clusters then shows that facets should occur parallel to these strong bonds, *i.e.* perpendicular to a few reciprocal quasi-lattice directions [equation (7)].

Alternative models for the structures of quasicrystals have been proposed, in which BOO is retained, but which lack positional order [the icosahedral glass model (Stephens & Goldman, 1986) and random tiling models (Henley, 1991)]. Such structures are possible as a random network of clusters, with the cluster-to-cluster bond in a definite orientation but without long-rang positional order. Considerations similar to those presented above show that BOO systems should have facets with the normal vectors perpendicular to the

bonds connecting clusters. The cluster-to-cluster contacts will be a very simple high-symmetry set, *e.g.* contacts or 'bonds' between clusters only occur along the twofold axes of the icosahedral group. The experimental observation of facets on quasicrystals perpendicular to the directions of twofold, threefold, and fivefold symmetry (Shen *et al.*, 1997) then shows that long-range order in quasicrystals does exist and that quasicrystalline structures cannot be described by a random aglomeration of clusters.

6.2. *Modulated and composite crystals*

Incommensurately modulated crystals usually exhibit normal facets with a surface normal parallel to a reciprocal-lattice vector of the average structure. In addition, satellite facets may be found, which can only be indexed with four or more integers (1) (Janner *et al.*, 1980). The mechanism of the stabilization of the normal facets is the same as for periodic crystals. For low-index directions of the lattice of the average structure, cutting of strong bonds can be avoided and these will be the stable facets. The stabilization of satellite facets is due to pinning of the phase of the modulation at the surface (van Smaalen, 1993). In §4, an extension of the theory has been given to include crystals with bonds in arbitrary directions.

Incommensurate intergrowth compounds can be considered as the coherent intergrowth of two or more incommensurately modulated structures. Similar mechanisms of stabilization are found to those for modulated crystals. They comprise the possibility to optimize the position of the cutting plane and the possibility to optimize the incommensurate phase parameter at the surface. Complications arise because a facet characterized by $(3 + d)$ small indices (1) can be of different character for the various subsystems (§5). Further complications are encountered because the bonds between atoms belonging to different subsystems do not have an average direction or an average length (§5.1). It was thus necessary to construct the surface free-energy density as a sum of contributions of the bonds within subsystems and the bonds between subsystems (§5.2).

Detailed reports do not exist on the morphology of composite crystals. Intergrowth compounds can be classified into a few structure types. Layered structures are represented by the inorganic misfit layer compounds (Wiegers, 1996). The crystals are usually platelets, with the most important facets parallel to the layers. Because the incommensurate direction is parallel to the layers too, this is a normal facet for both subsystems. Strong bonds exist within the layers, while weaker bonds are found between the layers and the stabilization is due to optimization of the position of the cutting plane: it always cuts between layers, thus avoiding cutting any strong intra-subsystem bonds [equation (40)]. The other

facets have not been characterized. Without more quantitative information about the strength of the different bonds, it is not possible to predict whether the other facets will be normal facets for one subsystem and satellite facets for the other [stabilized according to (41)] or that they will be satellite facets for all subsystems [stabilized according to (42)].

Urea inclusion compounds have hexagonal or pseudo-hexagonal symmetry. Urea molecules (the first subsystem) form a connected net, with (substituted) *n*-alkane molecules (the second subsystem) confined to channels parallel to the hexagonal axis (Harris & Thomas, 1990) (a channel-type intergrowth compound). The crystals have the shape of hexagonal columns, with the six hexagonally oriented facets being normal facets of both subsystems. A preliminary study of the facets at the ends of the columns did show only normal facets of the urea subsystem, which then are satellite facets of the second subsystem (Verheijen & van Smaalen, 1997). The strongest bonds are within the first subsystem, while bonds of secondary importance are between the two subsystems. The bonds within the second subsystem are weak. It is to be expected that the stabilization primarily involves avoiding cutting the strong bonds of the first subsystem. Because the bonds of secondary importance are between the subsystems, the most important facets are normal facets for both subsystems [equation (40)], in accordance with the observed morphology. Facets of secondary importance are the other normal facets of the first subsystem [equation (41)]. The possibility of satellite facets cannot be excluded by these considerations.

Finally, consider columnar intergrowth compounds. Each subsystem consists of columns or stacks of atoms or molecules, which are surrounded by columns of the other subsystem. Each subsystem has its own periodicity along the columns, thus providing the incommensurate direction (*e.g.* chosen as $\mathbf{a}_{1,3}$ and $\mathbf{a}_{2,3}$). Strong bonds (type *A*) within the subsystems are on the average parallel to the columns. Other strong bonds (type *B*) are only possible between the subsystems, and they may form a three-dimensionally connected net. If type-*A* bonds dominate $\gamma(\hat{\mathbf{n}})$, most stabilization is again obtained from the terms $\gamma_H^v(\hat{\mathbf{n}})$ and the most important facets will be normal facets for both subsystems [equation (40)]. If type-*B* bonds dominate the surface free energy, $\gamma_H^{vv'}(\hat{\mathbf{n}})$ or $\gamma_M^{vv'}(\hat{\mathbf{n}})$ are the most important contributions. Again, the common normal facets provide the best possibility to minimize $\gamma(\hat{\mathbf{n}})$ [equation (40)]. For the facets of secondary importance, it cannot be predicted whether the facets that are normal facets for one subsystem [equation (41)] or the facets that are true satellite facets [equation (42)] are the most stable ones.

7. Conclusions

The orientation dependence of the surface free-energy density $\gamma(\hat{\mathbf{n}})$ has been derived from the broken-bond

model for crystals, quasicrystals, incommensurately modulated crystals and intergrowth compounds. It is found that the stabilization of the so-called normal facets on periodic and aperiodic crystals is due to avoidance of cutting strong bonds, which is only possible for directions corresponding to $(3 + d)$ small integers. Satellite facets are stabilized by pinning the phase of the modulation at the surface.

The morphology of crystals and quasicrystals can be used to distinguish between systems that have long-range positional order and systems that lack this type of order, while retaining bond-orientation order (BOO). The observed morphology of quasicrystals is in accordance with positional order and it cannot be explained by BOO only.

Different types of intergrowth compounds exist, for which the distribution of strong and weak bonds is different. It is shown in §6.2 that, independent of this distribution, the most stable facets are always the normal facets common to the subsystems. An understanding of this feature can again be derived from the fact that cutting strong bonds can be avoided for facets that are commensurate with the lattice periodicity of those bonds. For bonds within a subsystem, a normal facet is the most stable one and a normal facet common to all subsystems then is favorable for all subsystems, thus allowing maximum stabilization. The bonds between subsystem do not have translation symmetry. However, if full coordination shells of the atoms are considered, the bonds between subsystems appear to have the translation symmetries of both subsystems. The period of the subsystem prevails, of which the atoms are at the surface. Again, maximum stabilization is found for the normal facets common to the subsystems. These facets should be the most important facets on any intergrowth crystal, in accordance with the sparse experimental information. Facets of secondary importance are the normal facets of the subsystem with the strongest bonds. True satellite facets will have the highest probability to be stable on intergrowth compounds of the column type.

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