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On the determination of step energies. Theoretical considerations and application to an anisotropic Kossel model

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Steps on surfaces are important in crystal growth theory, as the step free energy determines the two-dimensional nucleation rate, island growth, step flow and spiral growth. In this paper, it is illustrated that in general in lattice models the step energy of a single step cannot be determined directly by counting broken bonds. A new method is proposed that uses the geometry of a step together with the bonding topology, allowing for a straightforward determination of single-step energies for any case. The method is applied to an anisotropic Kossel model.

1. Introduction

Models for crystal morphology prediction date back to the 19th century, in which Bravais and Friedel, followed by Donnay and Harker, developed the theory nowadays known as the BFDH theory (Donnay & Harker, 1937, 1961). This theory states that, when taking into account certain symmetry arguments, the morphological importance of a crystallographic face (*hkl*) is proportional to the interplanar distance d_{hkl}. Although only the lattice parameters are considered, this theory works quite well for crystal structures with isotropic interactions.

In the 1950s, the attachment-energy theory was introduced by Hartman and Perdok, and later refined by Bennema and Hartman (Hartman & Perdok, 1955*a*,*bc*; Hartman & Bennema, 1980). In this theory, the crystal structure and bonds are taken into account. It relates the attachment energy of crystal slices of orientation (*hkl*) to the morphological importance of that orientation. Generally, if the attachment energy released upon growing a slice with thickness d_{hkl} is high, the growth rate in that direction will be high as well.

The Hartman–Perdok theory considers the energy of flat faces, but it is well known that in the actual crystal growth process, steps are more important than the flat terraces. Indeed, for several crystals with a needle morphology, it has been shown that the Hartman–Perdok approach fails and that the step structure is essential for understanding the morphology (Cuppen *et al.*, 2004, 2005; Deij *et al.*, 2005). Therefore, in this paper, we no longer look at the attachment energy between faces, but at the energies of steps *on* these faces.

Steps on surfaces play a fundamental role in crystal growth. Apart from rough growth for surfaces that have the step free energy $\gamma_{\rm st}(\mathbf{u}) + \gamma_{\rm st}(-\mathbf{u}) \leq 0$ for one or more step-front orientations $\mathbf{u}$ (van Beijeren & Nolden, 1987), the three main growth mechanisms all involve steps. Firstly, on a misoriented surface, step flow determines the growth. Secondly, when growth is taking place on a perfectly flat surface, two-dimensional nucleation and layer-by-layer growth is observed. Lastly, when a screw dislocation is present in the surface, the resulting spiral growth pattern emerges from a continuous step source. For all these mechanisms, the free energy of the steps plays a central role in the description of crystal growth (Burton *et al.*, 1951; van der Eerden, 1993).

Most of the crystal growth mechanisms have been studied using one of the simplest crystal models, the Kossel model (Kossel, 1927). Other models have been applied successfully to the understanding of equilibrium surface phase diagrams, like the body-centred solid on solid (BCSOS) model for crystals containing two growth units in the unit cell (den Nijs & Rommelse, 1989; Mazzeo *et al.*, 1995; Grimbergen *et al.*, 1999).

Real crystals, however, usually have more complex structures, often with more than one growth unit in the unit cell and with different bonds, resulting in various step configurations. The Kossel model and derived theories have limited applicability to these crystal structures. The growth involves multiple growth unit incorporation barriers, different for each incorporation site configuration. Also, the order in which the different growth units incorporate, affects the overall energetics profile, and multiple pathways to the same structure can have very different energetics associated with them. This is reflected in a large set of possible step structures. The first approach in dealing with this complexity would be to calculate the step energies of straight single steps, which would be the step free energy at zero Kelvin.

Although we are currently capable of simulating crystal growth for any crystal structure in any crystallographic orientation (Boerrigter *et al.*, 2004), these simulations give no fundamental insight into the processes taking place. The aim of the present research is therefore to develop methodology to calculate single-step energies for any crystal structure in any

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crystallographic orientation and to use the information obtained to come to a fundamental understanding of the crystal growth process in terms of step energies and two-dimensional nucleation barriers. First, however, in this paper, it will be shown that a direct and unique determination of single-step energies is impossible in many cases. This is shown for a low-symmetry orientation in an anisotropic Kossel model. The inability to assign step energies in this model has already been reported by Akutsu and coworkers, when studying an Ising antiferromagnet in an external field (Akutsu & Akutsu, 1995). As a solution, we propose a method which uses the geometry of a step on a given surface and given crystal structure. This method enables us to calculate the energy of a single step. For the determination of step energies for lattice models of any crystal structure, we have developed a computer program called *Steplift*, which will be introduced in a forthcoming paper (Deij *et al.*, 2006).

2. Determination of step energies

In this paper, the determination of step energies is performed within the framework of lattice models. These models use a number of implicit assumptions. First of all, the lattice nature of the model implies that the surface has a bulk termination, *i.e.* relaxation and reconstruction are not taken into account. Secondly, when bonds are broken between particles in a lattice model, the broken bond energy is divided equally between the two particles. When a surface is created by cleaving a crystal, both interfaces will have the same interfacial energy. The convention used in this paper is to denote ϕ as the energy of a broken bond per particle. This means that if one bond between two particles is broken, both particles gain ϕ in energy. A last assumption made in this paper is that all step configurations are calculated at zero Kelvin, implying zero kink density. In other words, entropy is ignored. As the step free energy has both a positive energetic contribution $\varepsilon_{\rm st}$, and a negative entropic contribution $s_{\rm st}$, a positive step free energy at non-zero temperatures depends on the existence of a positive $\varepsilon_{\rm st}$. Therefore, we look at step energy alone as an approximation for the step free energy. This approximation is expected to be better for conditions for which the kink density is small, *i.e.* at relatively low temperature and supersaturation.

2.1. Calculation of single-step energies

As was already briefly mentioned, a surface will have a non-zero roughening transition temperature if the sum of the energies of two opposing steps is greater than zero:

$$\gamma_{\rm st}(\mathbf{u}) + \gamma_{\rm st}(-\mathbf{u}) > 0 \;\; \forall \mathbf{u}, \;\; \mathbf{u}\cdot\mathbf{k} = 0, \tag{1}$$

with $\mathbf{k}$ the surface normal. However, to determine the optimal shape of a two-dimensional island with minimal step energy, the step energy of opposite steps has to be calculated individually.

This can be seen in Fig. 1. Here two situations are shown, in which the sum of the step energies ε_1 and ε_2 is equal in both cases. In Fig. 1(*a*), $\varepsilon_1 = \varepsilon_2$, whereas in Fig. 1(*b*), $\varepsilon_1 < \varepsilon_2$. The result is that the shape of the two-dimensional island changes due to the difference in single-step energies ε_1 and ε_2. Therefore, a method for the determination of energies of single steps is needed.

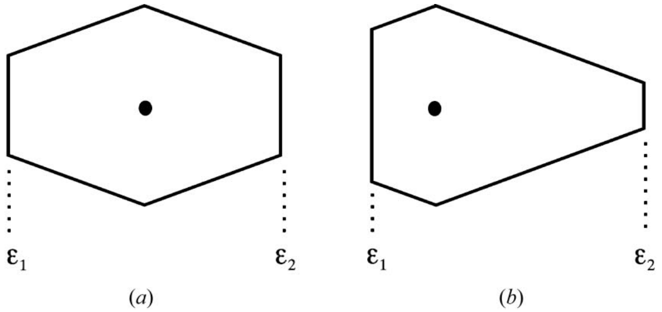

Figure 1
Two situations in which the sum of the step energies $\varepsilon_1 + \varepsilon_2$ is equal, but their individual contributions are different. (*a*) shows the situation where $\varepsilon_1 = \varepsilon_2$, while in (*b*) $\varepsilon_1 > \varepsilon_2$. The black dot indicates the origin of the Wulff shape.

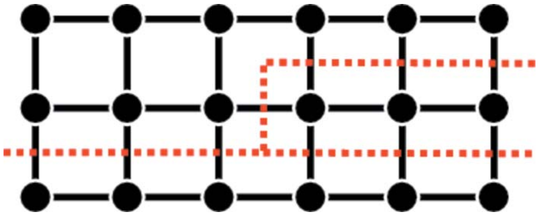

Figure 2
Direct determination of step energies in a Kossel crystal, viewed in a projection along the **a** axis The determination of the energy of this single step is performed by subtracting the number of broken bonds of the flat contour from the number of broken bonds of the stepped contour, giving the step energy as $\varepsilon_{\rm st} = \phi$.

For simple systems, like the Kossel crystal, single-step energies can be calculated directly. This is illustrated in Fig. 2 and is the ‘traditional’ method to determine step energies (Grimbergen *et al.*, 1998). When the stepped and unstepped surfaces have broken bonds of the same strength at the same lateral position, the step energies can be calculated by subtracting the number of broken bonds of the unstepped surface from the number of broken bonds of the stepped surface. As the same type of bonds are broken on the unstepped surface and on the lower and upper terrace of the stepped surface, the only extra broken bond is located at the step front, giving the step energy of one broken bond, ϕ, per unit cell. In the next section, an example will be given where the bonds broken on the stepped surface are not located at the same lateral position as the bonds broken on the unstepped surface, leading to the inability to calculate single-step energies directly, *i.e.* by just counting broken bonds.

2.2. Low-symmetry surface: $(0\bar{1}1)$ of an anisotropic Kossel model

We will use an anisotropic Kossel model which is just complex enough to illustrate the problem of the determination of single-step energies directly. The crystal graph of this anisotropic Kossel model is displayed in Fig. 3. A crystal graph

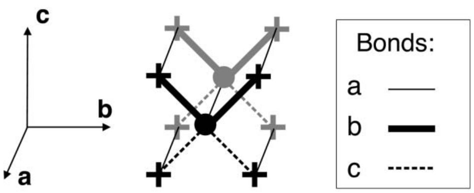

Figure 3
The anisotropic Kossel model crystal graph.

is a mathematical graph representation of the crystal structure: growth units are represented by graph vertices; pair-wise interactions between growth units by weighted undirected graph edges, as known from mathematical graph theory. There are three types of bonds in the model, a, b and c, with associated bond strengths ϕ_a, ϕ_b and ϕ_c, having $\phi_a = \frac{1}{2}(\phi_b + \phi_c)$. The anisotropy parameter δ is defined through $\phi_b = \delta\phi_c$ and is chosen in such a way that the $\delta = 1$ situation describes the classical Kossel model.

The steps with step-front directions [011] and $[0\bar{1}\bar{1}]$ on the $(0\bar{1}1)$ surface will be discussed next to illustrate the inability of the direct determination of single-step energies. Due to the symmetry of the system, this also holds for the [011] and $[0\bar{1}\bar{1}]$ steps on the $(01\bar{1})$ surface and the $[0\bar{1}1]$ and $[01\bar{1}]$ steps on the (011) and the $(0\bar{1}\bar{1})$ surfaces.

First note that the formation energy of an infinitely elongated island, involving two opposing steps ('up' and 'down'), can always be calculated directly, using the 'traditional' method of subtracting the broken bond energy of a flat surface from that of the surface with the two opposing steps. However, as was already pointed out before, to determine the optimal shape of a two-dimensional island, single-step energies are needed. The problem with determining these single-step energies directly is illustrated in Fig. 4. The figure displays an island viewed along the **a** axis, infinitely elongated in that direction. The formation energy of the island (*i.e.* the sum of the 'up' and the 'down' step) per unit length of the **a** axis is calculated by subtracting all broken bonds of a flat surface [in Fig. 4(*a*): $6(\phi_b + \phi_c)$] from the broken bonds of the doubly stepped surface ($8\phi_b + 6\phi_c$), giving an island formation energy of $2\phi_b$.

Next in Fig. 4, the island is cut at either a horizontal ϕ_c bond (Fig. 4*b*) or at a horizontal ϕ_b bond (Fig. 4*c*). One of the newly formed islands is shifted one unit cell to the right and the total energy is calculated for the two islands formed. In Fig. 4(*b*), this results in two islands, one having a net energy of $2\phi_c$ and the other of $2\phi_b$. The increase in total net energy with respect to the original island (*a*) is $2\phi_c$. The same procedure can be followed for breaking extra ϕ_b bonds (Fig. 4*c*), and in this case the extra energy is $2\phi_b$. In both situations, two new steps are created, and the simplest choice is to distribute the extra energy equally between both steps. This choice results in the following step energies for the four steps in Fig. 4(*d*): $\varepsilon_{\rm st,d1} = \varepsilon_{\rm st,d4} = \phi_c$ and $\varepsilon_{\rm st,d2} = \varepsilon_{\rm st,d3} = \phi_b$. That this is not correct can be seen from the fact that the original island in Fig. 4(*a*) is built up from two steps, d1 and d3, which would lead to a total island energy of $\phi_b + \phi_c$, a result that is in disagreement with the value $2\phi_b$ derived directly by counting the difference in broken-bond energy.

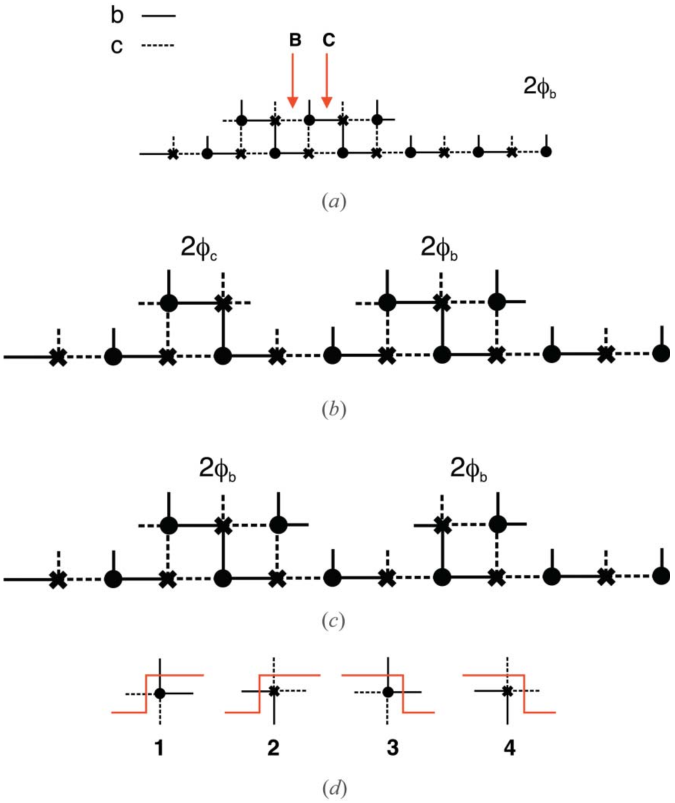

Figure 4
Ambiguity in the assignment of step energies to the [011] and $[0\bar{1}\bar{1}]$ steps on the $(0\bar{1}1)$ orientation of the anisotropic Kossel model. Two extra steps are created by cutting an existing island (*a*) either at location 'B' or at 'C'. The new islands, displayed in (*b*) and (*c*), respectively, give an extra energy of $2\phi_c$ and $2\phi_b$. When this extra energy is divided evenly over the steps created, the four steps displayed in (*d*), d1 to d4, become either ϕ_c or ϕ_b. However, this distribution of step energy is not correct. This can be seen in the island (*a*), which has two steps, d1 and d3. When the island energy of (*a*) is calculated as the sum of these two step energies, the island energy would become $\phi_b + \phi_c$, and it clearly is $2\phi_b$. Therefore, the equal distribution of the broken bond energy over the steps created is not correct.

The solution to this problem is shown in Fig. 5. In this figure a situation is shown in which first the step energies of two steps of double height are calculated directly (Fig. 5*a*). The energy of these individual double-height steps can be calculated by virtue of the fact that there is a perpendicular lattice vector between the upper terrace and the lower terrace, which means that all bonds that stick out from the upper terrace are also sticking out from the lower terrace at the same lateral position (*i.e.* the condition for calculating step energies directly). The step energy is then simply equal to the bonds that are broken at the side of the step, *i.e.* $\phi_b + \phi_c$. Next, in Figs. 5(*b*)–5(*e*), the single steps are calculated by creating two steps of single height, leading again to a situation in which a perpendicular lattice vector exists between the lower terrace and the uppermost terrace, which allows for the cancellation of broken bonds at the lower and uppermost terrace. This is done for the two single 'up' steps [type d1 in Fig. 5(*b*) and type d2 in Fig. 5(*c*)] and two single 'down' steps [type d3 in Fig. 5(*d*) and

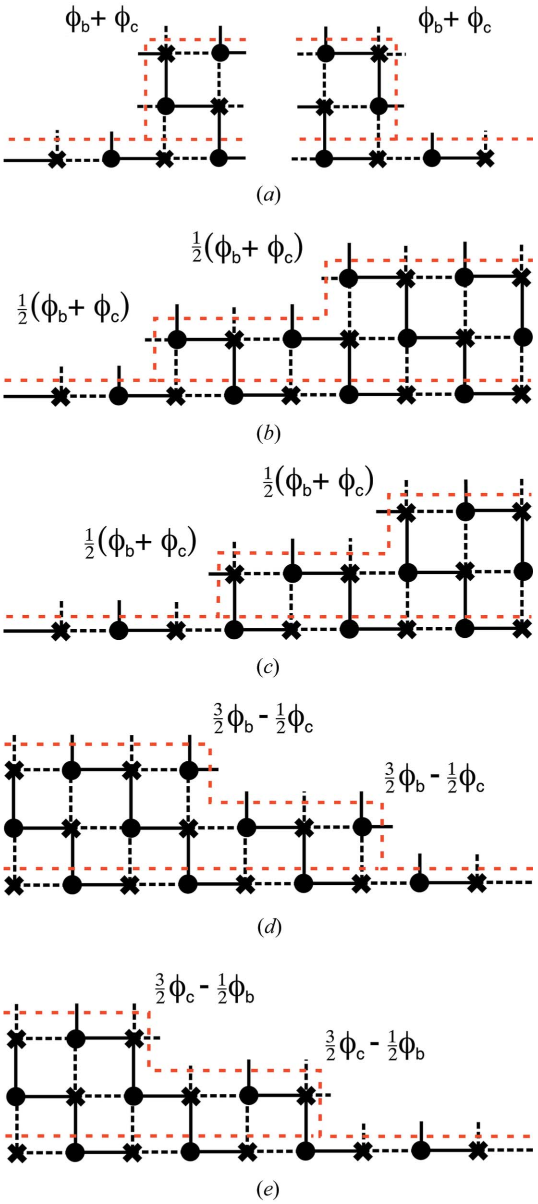

Figure 5
The step energy of steps of double height can be calculated directly due to the presence of a perpendicular lattice vector between the top and bottom terrace. The step energy of all steps of double height is equal to $\phi_b + \phi_c$ for both double-height steps. Next, in the lower four figures, two steps of single height are created to obtain the same bonds at the same lateral position on the lower terrace and the uppermost terrace. The energy of each single step can be determined to be $\frac{1}{2}(\phi_b + \phi_c)$ for the first two single steps, and $\frac{3}{2}\phi_b - \frac{1}{2}\phi_c$ and $\frac{3}{2}\phi_c - \frac{1}{2}\phi_b$ for the third and fourth single step, respectively.

type d4 in Fig. 5(*e*)]. Since the two single steps are identical, the energy of a single step is simply half the total energy. This brings us to the correct solution of $\varepsilon_{\rm st,d1} = \varepsilon_{\rm st,d2} = \frac{1}{2}(\phi_b + \phi_c)$ for the 'up' steps, and $\varepsilon_{\rm st,d3} = \frac{3}{2}\phi_b - \frac{1}{2}\phi_c$ and $\varepsilon_{\rm st,d4} = \frac{3}{2}\phi_c - \frac{1}{2}\phi_b$ for the two 'down' steps in Fig. 4(*d*).

3. Step geometry

In the previous section, the ambiguity for determining step energies directly was illustrated using an example of the [011] and $[0\bar{1}\bar{1}]$ steps on the $(0\bar{1}1)$ orientation of an anisotropic Kossel model. A solution was found by looking at steps of double height, so that the upper and lower terraces are the same, *i.e.* there is a perpendicular lattice vector between the upper and lower terrace. In the general case, it may take several individual steps before the upper and lower terraces are the same, but once this is achieved, the energy of an individual step can be determined.

In this section, a general method will be introduced to determine step energies of single-height steps, by taking the step terrace geometry into account. First the conditions for determining single-step energies directly are treated.

3.1. Conditions for determining single-step energies directly

Single-step energies on an (*hkl*) surface with a step height equal to the interplanar distance d_{hkl} can be calculated directly when there is a direct lattice vector $\mathbf{n}$ of length d_{hkl}, perpendicular to the surface (*hkl*).

The indices (*hkl*) refer to the reciprocal-lattice vector $\mathbf{k}_{hkl}$, normal to the (*hkl*) surface, which is defined as

$$\mathbf{k}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \tag{2}$$

with $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ the reciprocal-lattice vectors. The length of the vector $\mathbf{k}_{hkl}$ is then $1/d_{hkl}$, where d_{hkl} is the interplanar distance of the (*hkl*) surface. The set Λ of direct lattice vectors $\mathbf{m}$ is given by

$$\mathbf{m} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}, \quad u, v, w \in \mathbb{Z}, \tag{3}$$

with $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ the direct lattice vectors. Therefore, step energies can be calculated directly if there is $\mathbf{n} \in \Lambda$ satisfying

$$\Lambda \ni \mathbf{n} = d_{hkl}^2 \mathbf{k}_{hkl}. \tag{4}$$

Conversely, when there is no perpendicular lattice vector of length d_{hkl}, single-step energies cannot be calculated directly, unless two opposing steps are identical due to symmetry.

3.2. Determining step energies through symmetry

Step energies can also be calculated directly when there exists a mirror plane or a twofold axis perpendicular to the surface. In these cases, two opposite steps can be created that have a similar configuration by virtue of the symmetry in the system, and hence both steps will contribute equally to the island energy. A mirror plane can be present in systems without a translational vector perpendicular to the surface, for instance in the space group *Cm* at the (200) surface. An example of that situation is displayed in Fig. 6, which has two steps for which the energy can be determined to be $\frac{3}{2}\phi$ and $\frac{1}{2}\phi$. In space groups of higher symmetry, both perpendicular translational symmetry and a mirror plane or twofold axis can be present at the same time. While the use of symmetry can thus allow for a direct derivation of the energy of an individual step for such special cases, the same result is obtained by using the general approach described next.

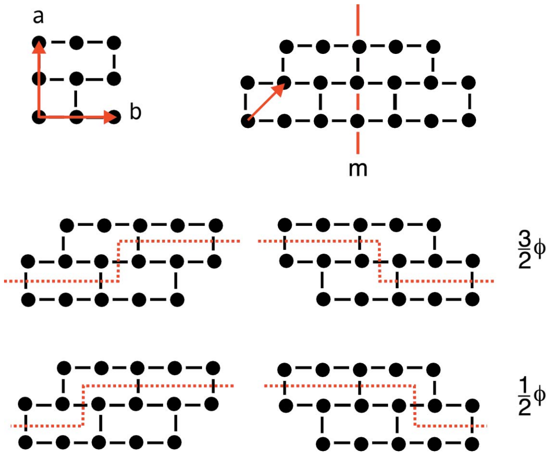

Figure 6
The top left figure displays a unit cell of a structure with space group *Cm*. This is a case where there is no perpendicular translational symmetry between (200) surfaces [a (200) translational symmetry vector, $\frac{1}{2}(\mathbf{a}+\mathbf{b})$, is indicated by the red vector in the top right figure). There is a mirror plane perpendicular to **b** and parallel to **c**, and due to this mirror symmetry the steps (left and right) in the middle and bottom figure are equivalent, and their energy can be calculated to be $\frac{3}{2}\phi$ (middle) and $\frac{1}{2}\phi$ (bottom).

3.3. A general approach

The general approach to calculate single-step energies uses the given crystal's geometry in addition to the bonding topology. Without losing generality, this approach uses a unit cell with the **a** and **b** axes defining the surface plane of interest, *i.e.* (001). Any surface (*hkl*) can be transformed into (001) by a proper choice of axis transformation. The resulting unit cell is called a slice cell, and its axes will be labeled $\mathbf{a}_s$, $\mathbf{b}_s$ and $\mathbf{c}_s$ (Boerrigter *et al.*, 2004). The slice cell transformation is chosen in such a way that the $\mathbf{a}_s$ vector lies parallel to the step front. As $\mathbf{a}_s$ and $\mathbf{b}_s$ lie in the plane of interest, $\mathbf{c}_s$ has the only perpendicular component with respect to the surface.

As was already shown in Fig. 5, for a single step a perpendicular lattice vector of length d_{hkl} allows for a direct calculation of its step energy. If there is no such perpendicular lattice vector for a step of single height, we can proceed by constructing a perpendicular lattice vector for a multiple-height step, satisfying

$$(w\mathbf{c}_s)_\perp = wd_{hkl}^2\mathbf{k}_{hkl} \simeq \mathbf{n} \in \Lambda \tag{5}$$

for some integer number w. Clearly, for some crystals, $(w\mathbf{c})_\perp$ may not be exactly equal to a lattice vector for any w, but it can be chosen arbitrarily close to a lattice vector **n**. Now, for a step of height w, all bonds that were broken at the lower terrace are also broken at the same lateral position on the upper terrace w layers higher, which means that their energies cancel exactly, allowing for the calculation of the total step formation energy.

To create a construction with w similar single steps, as shown in Fig. 7, the $\mathbf{b}_s$ axis is used v times. Any convenient value for v is allowed. The total translation is then given by the lattice vector $(v\mathbf{b}_s + w\mathbf{c}_s)$. The length of the vector product of the parallel component of this lattice vector with the vector $\mathbf{a}_s$ defines the total projected area under the full step structure A_total (see also Fig. 7):

$$\begin{aligned}
A_\text{total} &= \left|\mathbf{a}_s \times (v\mathbf{b}_s + w\mathbf{c}_s)_\parallel\right| \\
&= \left|\mathbf{a}_s \times [v\mathbf{b}_s + w(\mathbf{c}_s - \mathbf{c}_{s,\perp})]\right| \\
&= \left|\mathbf{a}_s \times \left\{v\mathbf{b}_s + w\left[\mathbf{c}_s - \frac{\mathbf{c}_s\cdot(\mathbf{a}_s\times\mathbf{b}_s)}{|\mathbf{a}_s\times\mathbf{b}_s|^2}(\mathbf{a}_s\times\mathbf{b}_s)\right]\right\}\right| \\
&= w\left|\mathbf{a}_s \times \left[\frac{v}{w}\mathbf{b}_s + \mathbf{c}_s - \frac{\mathbf{c}_s\cdot(\mathbf{a}_s\times\mathbf{b}_s)}{|\mathbf{a}_s\times\mathbf{b}_s|^2}(\mathbf{a}_s\times\mathbf{b}_s)\right]\right|.
\end{aligned} \tag{6}$$

Now, to calculate the formation energy of w identical steps in this construction, we use the following equation:

$$wE_\text{step} = E_w - A_\text{total}\mathcal{E}_\text{surf}, \tag{7}$$

where E_w is the total broken-bond energy of the surface with the w steps. This energy is well defined because the upper and lower terrace are identical. The specific surface energy $\mathcal{E}_\text{surf}$ is given by

$$\mathcal{E}_\text{surf} = \frac{E_s}{|\mathbf{a}_s \times \mathbf{b}_s|} \tag{8}$$

where E_s is the surface energy per slice cell for a step-free surface.

The structure shown in Fig. 7 can also be understood in terms of a vicinal surface along the translational vector $(v\mathbf{b}_s + w\mathbf{c}_s)$, so that the E_w term in equation (7) is equal to the vicinal surface energy. The vicinal surface energy must, however, be taken with respect to the underlying flat surface area, A_total, not the area of the vicinal surface, which would be equal to $|\mathbf{a}_s \times (v\mathbf{b}_s + w\mathbf{c}_s)|$.

Since the total step energy given in equation (7) consists of w identical individual steps, the energy of a single step is given by

$$E_\text{step} = \frac{E_w}{w} - \frac{A_\text{total}}{w}\mathcal{E}_\text{surf}. \tag{9}$$

Per step, the projected area A_st, is equal to

$$A_\text{st} = \frac{A_\text{total}}{w} = \left|\mathbf{a}_s \times \left[\frac{v}{w}\mathbf{b}_s + \mathbf{c}_s - \frac{\mathbf{c}_s\cdot(\mathbf{a}_s\times\mathbf{b}_s)}{|\mathbf{a}_s\times\mathbf{b}_s|^2}(\mathbf{a}_s\times\mathbf{b}_s)\right]\right|. \tag{10}$$

As E_w is built up from w contributions, E_w is written as

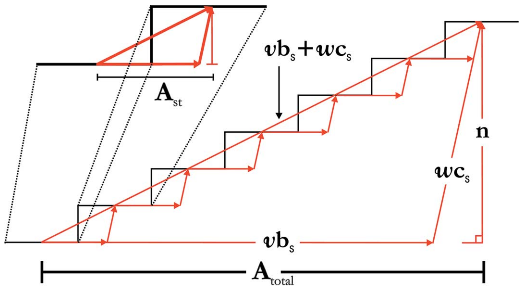

Figure 7
The construction of w steps (for w = 6) to let the perpendicular component of $w\mathbf{c}_s$ coincide with a lattice vector $\mathbf{n} \in \Lambda$ perpendicular to the surface. This choice, together with $\mathbf{a}_s$, defines the total area under the full step structure, A_total. In the left upper part, a single-step structure is enlarged to show the area under a single-step structure A_st.

$$E_w = wE_1 \qquad (11)$$

and using these expressions, the single-step formation energy becomes

$$E_{\text{step}} = E_1 - A_{\text{st}}\mathcal{E}_{\text{surf}}. \qquad (12)$$

Thus we find that the energy of a single step can be determined by first calculating the total energy of a surface with a single step and by subtracting from this the energy of the corresponding flat surface. The latter is the surface with the same projected area and with the specific surface energy $\mathcal{E}_{\text{surf}}$.

3.4. Application to the anisotropic Kossel model

The four steps discussed earlier are displayed in Fig. 8. For the two steps labeled '1' and '2', the slice cell basis vectors as defined in §3.3 are given by $\mathbf{a}_s = \mathbf{a}$, $\mathbf{b}_s = \mathbf{b} + \mathbf{c}$ and $\mathbf{c}_s = \mathbf{c}$. For the other two steps, '3' and '4', they are $\mathbf{a}_s = \mathbf{a}$, $\mathbf{b}_s = -(\mathbf{b} + \mathbf{c})$ and $\mathbf{c}_s = -\mathbf{b}$. In all figures displaying steps for this model, the step front lies along the $\mathbf{a}_s$ axis.

The red arrows in Fig. 8 (left) indicate the lattice vector $(\frac{v}{w}\mathbf{b}_s + \mathbf{c}_s)$, which is used for the definition of new periodic boundary conditions corresponding to a vicinal orientation, which includes the step of interest. The lattice vector $(\frac{v}{w}\mathbf{b}_s + \mathbf{c}_s)$ is, in all four cases, $3\mathbf{b}_s + \mathbf{c}_s$, with $v = 6$ and $w = 2$ [see equation (5)]. This results in A_{st} being equal to $\frac{7}{2}|\mathbf{a}_s \times \mathbf{b}_s|$, which expressed in the original lattice vectors is $\frac{7}{2}|\mathbf{a} \times (\mathbf{b} + \mathbf{c})|$ for all the steps.

The surface energy of the surface with the single step has to be calculated along the vicinal orientation, using periodic boundary conditions for the vicinal surface. The resulting energies are listed in Table 1. Using equation (12), the two $[0\bar{1}\bar{1}]$ steps both have a step energy of $\frac{1}{2}(\phi_b + \phi_c)$ and the two [011] steps have step energies of $\frac{3}{2}\phi_b - \frac{1}{2}\phi_c$ and $\frac{3}{2}\phi_c - \frac{1}{2}\phi_b$, respectively. This is, as expected, consistent with the results found for the earlier approach using steps of double height (see Fig. 5). For the island formation energy, combining an up and a down step, we find either $2\phi_b$ or $2\phi_c$, depending on the choice of the [011] step position, which is also consistent with the direct calculations on islands shown in Fig. 4. When the anisotropy factor δ equals 1, so that $\phi_b = \phi_c = \phi$, giving the classical isotropic Kossel model, the step energy becomes $E_{\text{step}} = \phi$ for all steps in Table 1. Hence, this method for determining single-step energies is also in accordance with the underlying Kossel model for $\delta = 1$.

Table 1
Step energies and individual contributions according to equation (12), calculated for the step configurations in Fig. 8.

$[uvw]$	E_w	A_{st}	$\mathcal{E}_{\text{surf}}$	E_{step}
1 $[0\bar{1}\bar{1}]$	$4(\phi_b + \phi_c)$	$\frac{7}{2}\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$(\phi_b + \phi_c)/\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$\frac{1}{2}(\phi_b + \phi_c)$
2 $[0\bar{1}\bar{1}]$	$4(\phi_b + \phi_c)$	$\frac{7}{2}\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$(\phi_b + \phi_c)/\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$\frac{1}{2}(\phi_b + \phi_c)$
3 [011]	$5\phi_b + 3\phi_c$	$\frac{7}{2}\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$(\phi_b + \phi_c)/\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$\frac{3}{2}\phi_b - \frac{1}{2}\phi_c$
4 [011]	$5\phi_b + 3\phi_c$	$\frac{7}{2}\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$(\phi_b + \phi_c)/\lvert\mathbf{a} \times (\mathbf{b} + \mathbf{c})\rvert$	$\frac{3}{2}\phi_c - \frac{1}{2}\phi_b$

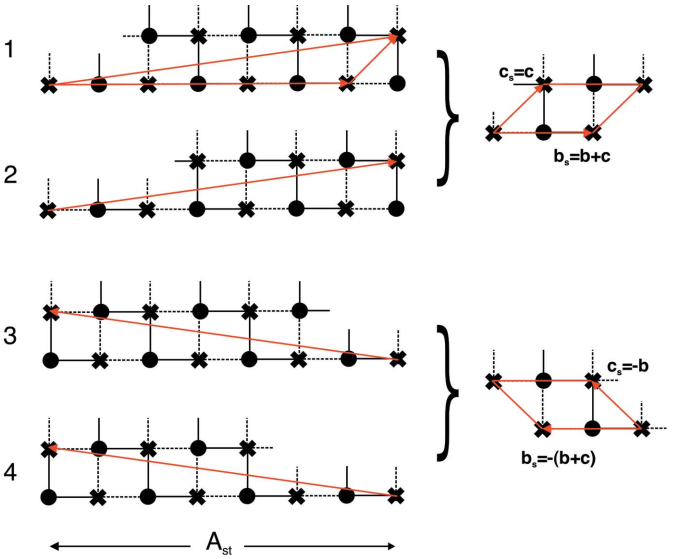

Figure 8
The four single steps in the [011] and $[0\bar{1}\bar{1}]$ directions on the $(0\bar{1}1)$ surface. The numbers correspond to those in Fig. 4(*d*). The slice cell used is displayed on the right and the red arrows on the left define the vector $(\frac{v}{w}\mathbf{b}_s + \mathbf{c}_s)$ which, projected on the lower terrace, gives A_{st}. In all cases, A_{st} is equal to $\frac{7}{2}|\mathbf{a} \times (\mathbf{b} + \mathbf{c})|$. The vectors $\mathbf{c}_s$ and $\mathbf{b}_s$ of the slice cells on the right are expressed in terms of the axes of the original unit cell in Fig. 3.

3.5. Application to a variable-angle anisotropic Kossel model

It is well known that crystallographic angles may vary, depending on, for instance, temperature or pressure. To investigate the effect of a varying angle, we now apply the method introduced previously to the model shown in Fig. 9. In this case we allow the slice cell angle α to be variable. It will be shown that the energy of single steps becomes angle-dependent, but that in any combination of two opposing steps the dependence on the angle vanishes.

Again, the specific surface energy $\mathcal{E}_{\text{surf}}$ is given by

$$\mathcal{E}_{\text{surf}} = \frac{(\phi_b + \phi_c)}{|\mathbf{a}_s \times \mathbf{b}_s|}.$$

The angle α can be expressed as

$$\tan\alpha = d_{hkl}/l,$$

where l is the length of the $\mathbf{c}_s$ axis projected on the $\mathbf{b}_s$ axis. This means that for the steps, shown in Fig. 9, the projected areas

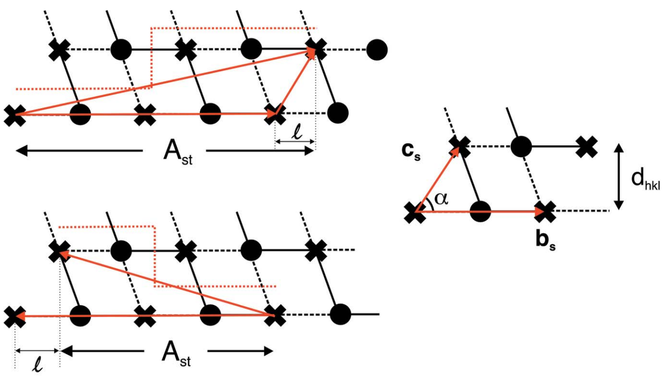

Figure 9
Dependence of step energy on the angle α.

are given by $A_{\rm st} = (2 + l/|\mathbf{b}_{\rm s}|)|\mathbf{a}_{\rm s} \times \mathbf{b}_{\rm s}|$ for the step up, and $A_{\rm st} = (2 - l/|\mathbf{b}_{\rm s}|)|\mathbf{a}_{\rm s} \times \mathbf{b}_{\rm s}|$ for the step down.

The step energies of the steps become

$$E_{\rm step,up} = 3(\phi_{\rm b} + \phi_{\rm c}) - (\phi_{\rm b} + \phi_{\rm c})\left(2 + \frac{d_{hkl}}{|\mathbf{b}_{\rm s}| \tan\alpha}\right)$$

and

$$E_{\rm step,down} = 3\phi_{\rm b} + \phi_{\rm c} - (\phi_{\rm b} + \phi_{\rm c})\left(2 - \frac{d_{hkl}}{|\mathbf{b}_{\rm s}| \tan\alpha}\right).$$

Combining the up and down step gives an energy of $2\phi_{\rm b}$, without a dependence on the angle.

4. Discussion

We have shown that the energy of a single step can be calculated directly and unambiguously only when a certain symmetry is present. This symmetry can be a perpendicular lattice vector, a mirror plane or twofold axis. In fact, such symmetry, present in many simple models, has facilitated the calculation of single-step energies in the past. Thus, in these cases, the geometry of the system was implicitly used in the calculation of step energies.

The method presented here is based on a perpendicular lattice vector, the presence of which makes the upper and lower terraces identical. This also means that our method is not applicable to steps that have different upper and lower terraces. Although crystals are usually terminated by similar surfaces below the roughening temperature, examples are known that do not have the same surface for the upper and lower terrace, for instance crystals with an A–B layered structure (Plomp *et al.*, 2000). In addition, crystals with interlaced step patterns (van Enckevort & Bennema, 2004) will need special attention.

In the framework of statistical physics, step energies are calculated based on bonding topology alone (Akutsu & Akutsu, 1995). When a crystal lattice parameter is altered, for instance a change in the angle α, as shown in §3.5, translational symmetry will be altered, and as a result the step energies change in our approach. This raises the question whether the step energy should be allowed to change when the crystal lattice is altered without any change in bonding topology. On the basis of the topology alone, this question should be answered negatively. However, when the crystal lattice is altered, the bond strengths may change as they are all a function of distance between interacting growth units. Thus, bonding topology and geometry are not independent in practice, and upon modification of the crystal lattice the step energy will therefore change both because of a change in geometry as well as a change in all the bond strengths.

The formation of kinks on steps is analogous to the formation of steps on surfaces, but one dimension lower: a straight step is analogous to a flat surface; a kink is analogous to a step on a surface. Our method can in principle be used to calculate kink energies. The roughening behaviour of steps is different, however: steps are always rough, as opposed to surfaces. The prerequisite that kinks should have the same lower and upper step front can therefore not always be fulfilled and, although kink energies can be calculated using the method, this can become very complicated in the general case.

One of the applications of the step energies, when calculated using our method, is to find the two-dimensional island with minimal step energy. As the single-step energies can always be determined using the geometric method, the shape of the island only depends on the magnitude of the step energies and the step-front orientations. The total island energy can be used as a measure for the nucleation barrier on a surface. When nucleation is the rate-limiting step for crystal growth, this result for the nucleation barrier can be used as a parameter to estimate the growth rate.

5. Conclusion

It has been shown that the step energy of steps lacking a perpendicular lattice vector of length d_{hkl} or any alternative appropriate symmetry cannot be determined directly. Using the geometry of the crystal in addition to the bonding topology, this problem was solved. For the anisotropic Kossel model it was shown that this method is both consistent with the energy of an island, *i.e.* two opposing steps, and with the limiting case of the Kossel model.

A result of our approach is that the step energies change when the geometry is distorted. From a statistical mechanical point of view, this is a remarkable result. We argue, however, that in reality bonding topology and geometry of crystals are closely connected. The geometry is determined by the bonding properties and, conversely, the bond strength will depend on the geometry.

The method put forward in this paper will be applied to a number of crystal structures studied experimentally in a forthcoming paper, in which an automated method for the determination of step energies is presented and applied to predict crystal morphology (Deij *et al.*, 2006).

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