ENERGIES OF SURFACE LEDGES AND KINKS

M. A. FORTES and J. BRITO CORREIA

Departamento de Engenharia de Materiais, Instituto Superior Técnico,
Av. Rovisco Pais, 1000 Lisboa, Portugal

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ABSTRACT — The description of the surface of a crystal in terms of terraces, ledges and kinks (TLK) is discussed , and equations are derived that determine the TLK content of the surface for any choice of terraces and ledges. The surface energy can be obtained as a sum of contributions of terraces, ledges and kinks. The form of the lattice sums that give these contributions in terms of a pairwise interaction potential is derived.

The accuracy of the TLK decomposition of surface energy is assessed by comparing the TLK energies with those calculated directly. Calculations were done for a f. c. c. crystal using three Mye potentials (6 | 9, 6 | 12 and 9 | 12) and limiting the choice of terraces and ledges to the more closely packed planes and directions, respectively. A very accurate method for calculating the lattice sums was developed, with which terrace, ledge and kink energies were determined. From these results it is concluded that the accuracy of the TLK decomposition of energy decreases as the range of the potential increases, but is never worse than one percent for the potentials used.

The analogy of the TLK description with the coincidence site lattice model of interfaces is emphasized.

1 – INTRODUCTION

At the atomic level, the simplest solid surfaces are those obtained in a monoatomic crystal by a cut parallel to a lattice plane, followed by removal of the atoms in one side of the cut. The atomic distribution of the atoms is then periodic in each of the planes parallel to the cut, even if relaxation of the atomic positions is taken into account. The surface atoms may be defined as those with potential energies, ε (in the field of the other atoms), exceeding a specified value, for example $|\varepsilon| < 0.99\,\varepsilon_c$, where ε_c is the cohesive energy. If the plane of the surface is a low index, high atomic density plane, the surface atoms will be, if the interaction is of short enough range, only those in the topmost plane. In this case, there is only one type of surface site (see example in Fig. 1a). However, for high index surfaces (Fig. 1b), the surface atoms will belong to a number of planes parallel to the topmost plane, although the thickness of the surface region should be comparable in both cases. For a high index surface, the properties (e. g. the energy) of the atoms vary slightly from plane to plane, in the surface region, so that, strictly, there are as many types of surface sites as parallel planes in the surface region. However, the change in energy from plane to plane is not in general uniform (broken bond model!), and it is formally convenient to group the atoms with similar properties in the same class. This then leads to the terrace-ledge-kink (TLK) description of the surface [1], which essentially recognizes only three types of surface atom sites (marked 1, 2 and 3 in Fig. 2a). The terraces are low energy, high atomic density planes. The ledges (or steps) are parallel to close packed directions and uniformly spaced; they can be regarded as monoatomic steps from one terrace to the next. The kinks are arranged in a planar lattice (that of the surface plane) and can be described as steps in the ledges. The energy of the surface atoms increases in the order terrace sites, ledge sites, kink sites.

This is the essence of the TLK model of a crystal surface, which has proved very useful in discussing properties such as surface and evaporation energies [2-4] and phenomena such as adsorption, surface diffusion and crystal growth [5]. Real surfaces do contain ledges and kinks, but not regularly distributed, and in general other types of atom sites will be found in them. In this paper, we shall consider only regular ideal surfaces obtained by a cut through a lattice plane, for which the TLK decomposition is periodic.

Formally, the TLK description can be applied to any orientation of the surface and to any choice of the plane of the terraces

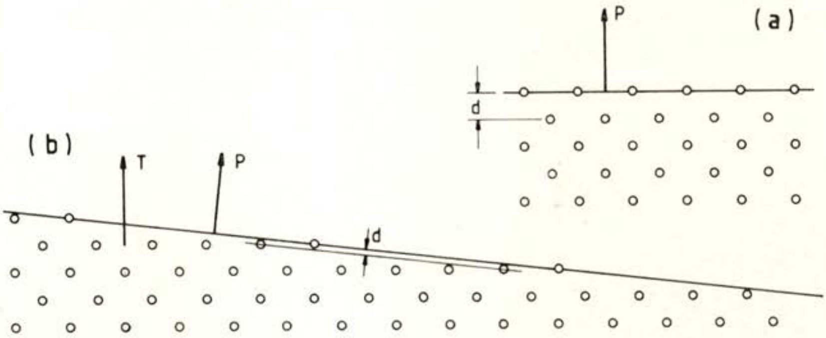

Fig. 1 — Different orientations of the surface "plane" **P** in a two-dimensional crystal: (a) low index, high atomic density; (b) high index, low atomic density. The interplanar spacings are indicated.

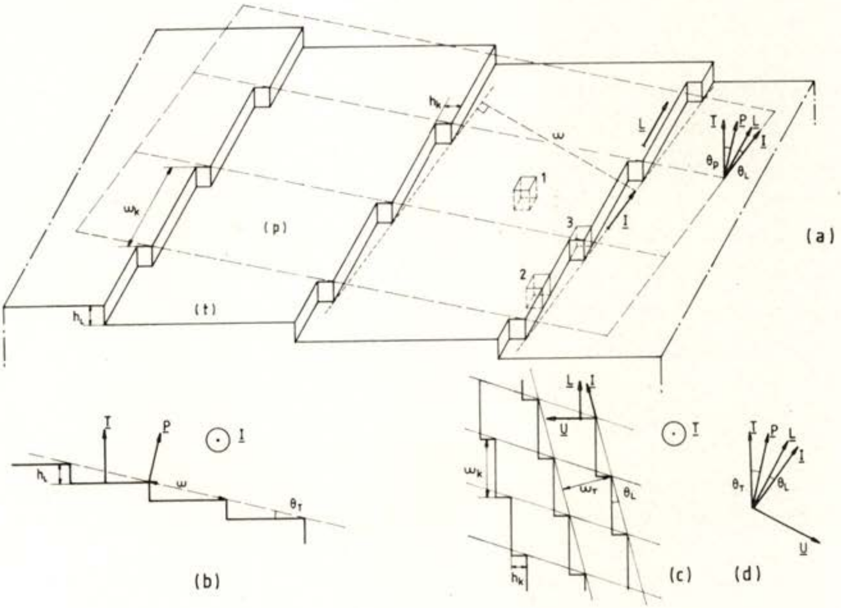

Fig. 2 — An arbitrary surface orientation (p) showing a TLK decomposition. The unit vectors normal to the surface plane (**P**) and to the terraces (**T**) are shown. **L** is a unit vector along the ledges and **I** a unit vector parallel to the intersection of planes **P** and **T**. Atoms 1, 2 and 3 are respectively at terrace, ledge and kink sites. Diagrams (b) and (c) are sections of (a) through planes perpendicular to **I** and **T**, respectively. Diagram (d) shows the vectors used in the text; **U**, **L**, **T** define a triorthogonal direct reference system.

and of the direction of the ledges. The spacing between ledges and that between kinks is then determined to give the specified orientation of the surface plane. However, as the orientation of the surface deviates more and more from that of the chosen terraces, the density of ledges and kinks increases so that their interaction becomes strong [6] and their individuality may become questionable. On the other hand, if the terraces are taken as high index planes, it is no longer legitimate to consider only one type of surface sites in the terraces. These limitations to the applicability of the TLK model will have a repercussion when one attempts to calculate overall surface properties, e. g. the surface energy, in terms of contributions due to terraces, ledges and kinks.

The present paper concentrates on this topic and contains a detailed study of the surface energy decomposition in terms of TLK, from which conclusions on the applicability of the TLK model can be drawn. We first write down the equations that give the TLK content of an arbitrary surface and for arbitrary orientations of the terraces and ledges. We then derive the lattice sums that give the contributions to the surface energy of ledges and kinks, assuming a pairwise interaction between the atoms. The properties of the sums are discussed and their actual calculation is done for a f. c. c. crystal using three potentials of the Lennard-Jones type (Mye potentials). The results are used to calculate surface energies of various planes from their TLK content. These surface energies are then compared with those obtained by a direct method [7], in order to assess the range of applicability of the TLK decomposition from the point of view of surface energy. No corrections associated with relaxation of the atoms to their equilibrium positions have been included in our calculations. As shown in the preceding paper, these corrections are always very small for the potentials that will be used here. A recent example of calculations of relaxed ledge energies in ionic crystals can be found in ref. 8.

The problems that we discuss are formally similar to those found in the coincidence site lattice (c. s. l.) model of grain boundaries [e.g. 9, 10]. In this model, the concept of special (or favoured) c. s. l. boundaries is the equivalent to low index surfaces, and the grain boundary dislocations are the equivalent to surface ledges and kinks, which can, in fact, be regarded as surface defects. On the other hand, the range of applicability of the c. s. l. model is limited by similar questions and can be assessed in similar grounds.

2 – DETERMINATION OF THE TLK DECOMPOSITION

Consider a surface in a crystal with one atom per lattice point, parallel to an arbitrary crystallographic plane with Miller indices $(p) \equiv (p_1 \, p_2 \, p_3)$ referred to a vector basis $\mathbf{e}_1 \, \mathbf{e}_2 \, \mathbf{e}_3$ (not necessarily a lattice basis). The unit normal to the plane is $\mathbf{P}$ and the interplanar spacing is d (Figs. 1 and 2).

The plane of the terraces is $(t) = (t_1 \, t_2 \, t_3)$ with unit normal $\mathbf{T}$. The ledges are parallel to the crystal direction $[l] = [l_1 \, l_2 \, l_3]$ with unit vector $\mathbf{L}$. The height h_L of the ledges is the interplanar spacing d_T of (t)

$$h_L = d_T \tag{1}$$

and the height h_K of the kinks is the distance between adjacent rows $[l]$ in the plane (t). Let i_L be the repeat distance along the ledges and v the volume per lattice point (atom). Then

$$h_K = \frac{v}{d_T \, i_L} \tag{2}$$

The angle $\Theta_T \, (0 \leqslant \Theta_T < \pi/2)$ between the plane of the surface (p) and the plane of the terraces (t) is given by

$$\cos \Theta_T = \mathbf{P} \cdot \mathbf{T} \tag{3}$$

The intersection of these two planes is a crystal direction $[i]$ of unit vector $\mathbf{I}$ at an angle Θ_L with the direction of the ledges $(0 \leqslant \Theta_L < \pi/2)$:

$$\cos \Theta_L = \mathbf{I} \cdot \mathbf{L} \; ; \quad \mathbf{I} \cdot \mathbf{P} = \mathbf{I} \cdot \mathbf{T} = 0 \tag{4}$$

The spacing between ledges, measured in the direction perpendicular to $\mathbf{I}$ in the plane (p) is $w = h_L / \sin \Theta_T$. The width w_T of the terraces (distance between ledges measured in the plane (t)) can be related to h_L (Fig. 2c):

$$w_T = h_L \, \mathrm{cotg} \, \Theta_T \cos \Theta_L \tag{5}$$

The distance between adjacent kinks in the same ledge, w_K, is measured along the ledge and is given by

$$w_K = h_K \operatorname{cotg} \Theta_L \tag{6}$$

All the quantities defined above are indicated in Fig. 2.

If **P** defines a lattice plane, as we are assuming, the distribution of ledges and kinks is periodic. The period corresponds to a unit cell in the plane (p), defined by the kink sites. The area of this unit cell is $w w_K / \cos \Theta_L$. The corresponding area of terrace is obtained by multiplying by $\cos \Theta_T$. The length of ledges in the period is w_K and there is one kink per period. Let γ be the surface energy of (p), γ_T the surface energy of the terraces (both per unit area), $_L$ the ledge energy per unit length and ε_K the energy of a kink. Then

$$\gamma \frac{w w_K}{\cos \Theta_L} = \gamma_T \frac{w w_K}{\cos \Theta_L} \cos \Theta_T + \varepsilon_L w_K + \varepsilon_K \tag{7}$$

Using eqs. 5 and 6 we finally obtain

$$\gamma = \gamma_T \cos \Theta_T + \frac{\varepsilon_L}{h_L} \sin \Theta_T \cos \Theta_L + \frac{\varepsilon_K}{h_L h_K} \sin \Theta_T \sin \Theta_L \tag{8}$$

with h_L and h_K given by eqs. 1 and 2, respectively.

In this approach, ledges and kinks are treated as line and point features on the surface, respectively. The surface itself is treated as a geometric surface. The approach is macroscopic in this respect. For example, the specific surface energy, γ_T, should be regarded as an average surface energy of the actual terraces, and possibly affected by their width. The TLK decomposition of the energy is acceptable for those planes such that the terrace and ledge energy is negligibly different from that of a wide terrace or of a ledge with no kinks, respectively.

We will now show how these limitations to eq. 8 can be put in more precise terms. This will be done by using an atomic approach to the surface energy, through which we are able to obtain the lattice sums with which terrace, ledge and kink energies can be calculated.

3 – LATTICE SUMS FOR LEDGE AND KINK ENERGIES

The derivation of the lattice sums for γ_T, ε_L and ε_K is based on the equation for the energy of a surface of arbitrary orientation in terms of the pairwise interaction between the atoms. For a potential $\varepsilon(\rho)$, where ρ is the distance between two atoms, the surface energy γ for the orientation defined by a plane $(p_1 p_2 p_3)$ of unit normal **P**, is [7]

$$\gamma = -\frac{1}{2v} \sum_{n} (\mathbf{n} \cdot \mathbf{P})\ \varepsilon(n)\ ;\ \mathbf{n} \cdot \mathbf{P} > 0 \qquad (9)$$

where v is the volume per atom and **n** defines the positions of the atoms relative to a reference atom; the sum is for all **n** such that $\mathbf{n} \cdot \mathbf{P} > 0$.

We define a unit vector **U** by the vector product

$$\mathbf{U} = \mathbf{L} \times \mathbf{T} \qquad (10)$$

L, **T** and **U** define a triorthogonal direct reference system (Fig. 2d). The vector **P** makes an angle Θ_T with **T** and its projection in the plane of **U** and **L** makes an angle with **U** which is equal to the angle Θ_L, between **l** and **L**. Therefore

$$\mathbf{P} = \mathbf{T} \cos \Theta_T + \mathbf{U} \sin \Theta_T \cos \Theta_L + \mathbf{L} \sin \Theta_T \sin \Theta_L \qquad (11)$$

with both Θ_T and Θ_L in the interval $(0, \pi/2)$. Combining eqs. 9 and 11 yields

$$\gamma = -\frac{1}{2v} [\cos \Theta_T \sum_{n} (\mathbf{n} \cdot \mathbf{T})\ \varepsilon(n) + \sin \Theta_T \cos \Theta_L \sum_{n} (\mathbf{n} \cdot \mathbf{U})\ \varepsilon(n)$$

$$+ \sin \Theta_T \sin \Theta_L \sum_{n} (\mathbf{n} \cdot \mathbf{L})\ \varepsilon(n)]\ ;\ \mathbf{n} \cdot \mathbf{P} > 0 \qquad (12)$$

The sums in eq. 12 are for all **n** such that $\mathbf{n} \cdot \mathbf{P} > 0$. When Θ_T and Θ_L tend to zero (the density of ledges and kinks tends to zero), the condition $\mathbf{n} \cdot \mathbf{P} > 0$ is equivalent to the following three alternative conditions: (i) $\mathbf{n} \cdot \mathbf{T} > 0$; (ii) $\mathbf{n} \cdot \mathbf{T} = 0$ and $\mathbf{n} \cdot \mathbf{U} > 0$; (iii) $\mathbf{n} \cdot \mathbf{T} = \mathbf{n} \cdot \mathbf{U} = 0$ and $\mathbf{n} . \mathbf{L} > 0$. In this limit, the sucessive sums in eq. 12 are calculated for the $\mathbf{n}$ that satisfy the sucessive conditions (i) to (iii). Comparing eq. 8 with eq. 12 we obtained the lattice sums for γ_T, ε_L and ε_K. The first has the expected form, analogous to eq. 9:

$$\gamma_T = -\frac{1}{2v} \sum_{\mathbf{n}} (\mathbf{n} \cdot \mathbf{T})\, \varepsilon(n) \; ; \; \mathbf{n} \cdot \mathbf{T} > 0 \tag{13}$$

The ledge energy is given by

$$\varepsilon_L = -h_L/(2v) \sum_{\mathbf{n}} (\mathbf{n} \cdot \mathbf{U})\, \varepsilon(n) \; ; \; \mathbf{n} \cdot \mathbf{U} > 0 \, , \; \mathbf{n} \cdot \mathbf{T} = 0 \tag{14}$$

and the kink energy by

$$\varepsilon_K = -h_L h_K/(2v) \sum_{\mathbf{n}} (\mathbf{n} \cdot \mathbf{L})\, \varepsilon(n) \; ; \; \mathbf{n} \cdot \mathbf{L} > 0 \, , \; \mathbf{n} \cdot \mathbf{T} = 0 \, , \; \mathbf{n} \cdot \mathbf{U} = 0 \tag{15}$$

The series for ε_L is a double sum (two subscripts) and that for ε_K is a simple sum (one subscript). Eqs. 14 and 15 give the energy of isolated ledges and kinks, respectively. Eq. 15 shows that the energy of a kink depends on the ledge where the kink is located, but not on the associated terrace.

A simple interpretation can be given to these equations. Eq. 14 is the expression that one would write to calculate the energy, per unit length, of a "surface" created in a crystal plane (t), of normal $\mathbf{T}$, by a cut along a direction $\mathbf{L}$. This energy is, apart from the sign, one half the potential energy of one half-plane in the field of the other half-plane, the two half-planes being separated along a direction $\mathbf{L}$. Calculating this energy by a process similar to that used to obtain surface energies, Eq. 14 would result, since the repeat distance along $\mathbf{L}$ multiplied by the inter-$\mathbf{L}$ direction spacing is v/h_L. Similarly, Eq. 15 gives the "surface" energy per atom of a row $\mathbf{L}$, the "surface" being created by separating the row into two halves. These interpretations of ε_L and ε_K could have been used to derive Eqs. 14 and 15. For example, two isolated parallel ledges can be created on the surface by separating the topmost plane into two half-planes, while keeping the half-planes at the same distance from the next plane. Eq. 14 would then result for the energy of an isolated ledge, per unit length. It is then apparent that the energies γ_T, ε_L and ε_K obtained from

Eqs. 13-15 are exact for the isolated or "pure" terraces, ledges and kinks, respectively. If those energy values are used to calculate energies of surfaces of any orientation, an error will result, which increases as the density of ledges and kinks increases, and, as will be shown below, as the atomic density in terraces and ledges decreases. An evaluation of these errors will be described in the following sections.

4 – APPLICATION TO F. C. C. CRYSTALS, MYE POTENTIALS

Taking a orthormal basis $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, with $|\mathbf{e}_i| = 1$, parallel to the cube edges of a f. c. c. cell, the general form of $\mathbf{n}$ is

$$\mathbf{n} = \frac{a}{2} \sum_i n_i \, \mathbf{e}_i \; ; \quad \sum_i n_i = \text{even integer} \tag{16}$$

where the n_i are integers with an even sum and a is the lattice parameter. For a plane with Miller indices $(p_1 \, p_2 \, p_3) = (p)$ we have

$$d = \frac{a}{p} \; ; \quad \mathbf{P} = \frac{1}{p} \sum_i p_i \, \mathbf{e}_i \; ; \quad p^2 = \sum_i p_i^2 \tag{17}$$

provided the p_i are chosen as all odd (coprime) integers or all even integers (g. c. d. equal to 2). The indices $[\, l_1 \, l_2 \, l_3 \,]$ of a lattice direction are chosen such that their sum is even; the repeat distance i_L along the direction is given by

$$i_L = \frac{a}{2} \, l \qquad l^2 = \sum_i l_i^2 \tag{18}$$

The interaction energy between two atoms will be described by a Mye potential $e \,|\, e'$:

$$\varepsilon(\rho) = \varepsilon_0 \left[\left(\frac{\sigma}{\rho} \right)^{e'} - \left(\frac{\sigma}{\rho} \right)^{e} \right] , \; e < e' \tag{19}$$

with $e, e' = 6$, 9 and 12; ε_0 can be related to the cohesive energy per atom in the crystal, ε_c, and σ to the near-neighbour distance, r_0 (see Table 1 in ref. 7). Eqs. 9 and 13 for the surface energies take the form that has been derived in ref. 7.

The ledge energy (eq. 14) becomes

$$\varepsilon_L = \frac{\sqrt{2}}{t\,u}\,\frac{\varepsilon_0}{r_0}\,\left(\sigma^{*e'}\,\Delta_{e'} - \sigma^{*e}\,\Delta_e\right) \tag{20a}$$

where

$$\sigma^* = \sqrt{2}\,\frac{\sigma}{r_0}\ ;\quad u^2 = \sum_i u_i^2\ ;\quad t^2 = \sum_i t_i^2 \tag{20b}$$

and

$$\Delta_e = \sum_{\mathbf{n}} \frac{m}{n^e} \tag{20c}$$

with

$$m = 1/2 \sum_i n_i\,u_i > 0\ ;\ \sum_i n_i\,t_i = 0\ ;\ n^2 = \sum_i n_i^2 \tag{20d}$$

The u_i are the indices of the lattice direction parallel to **U**.

For the energy of a kink we obtain from eq. 15

$$\varepsilon_K = \frac{\varepsilon_0}{l^2}\,\left(\sigma^{*e'}\,\Psi_{e'} - \sigma^{*e}\,\Psi_e\right)\ ;\ l^2 = \sum_i l_i^2 \tag{21a}$$

where

$$\Psi_e = \sum_{\mathbf{n}} \frac{m'}{n^e} \tag{21b}$$

with

$$m' = 1/2 \sum_i n_i\,l_i > 0\ ;\ \sum_i n_i\,t_i = \sum_i n_i\,u_i = 0\ ;\ n^2 = \sum_i n_i^2 \tag{21c}$$

l_i are the indices of the direction of the ledges. The sum Ψ_e can be written in a simpler form. Since **n** is parallel to **L** and $\mathbf{n} \cdot \mathbf{L} > 0$ we write

$$n_i = k l_i \qquad k \geqslant 1$$

where k is an integer. This leads to

$$\Psi_e = 1/2\ l^{2-e} \sum_{k \geq 1} \frac{1}{k^{e-1}} = 1/2\, l^{2-e}\ \phi_e \tag{22}$$

The actual calculation of the lattice sums Δ_e and Ψ_e is discussed in the Appendix.

5 – RESULTS

5.1 – *Ledge and Kink Energies*

Ledge and kink energies were calculated for f. c. c. Lennard-Jones crystals (potentials 6 | 9, 6 | 12 and 9 | 12) by the method described in the Appendix with $M = 10$ and $k_0 = 10$, respectively. Values of the calculated ledge energies are indicated in Table 1, in ε_c/r_0 units. The values are fairly similar for the three potentials. These data also show the effect of the associated terraces on the ledge energy. The ledge energy tends to decrease as the atomic density in the associated terrace decreases.

TABLE 1 — Ledge energies (ε_c / r_0 units)

Terrace	Ledge	Ledge energy		
		6 | 9	6 | 12	9 | 12
(111)	$[1\bar{1}0]$	0.1467	0.1500	0.1566
	$[11\bar{2}]$	0.1594	0.1658	0.1785
(002)	[110]	0.1075	0.1038	0.0962
	[200]	0.1179	0.1188	0.1207
	[130]	0.1208	0.1202	0.1192
(022)	$[01\bar{1}]$	0.0376	0.0299	0.0145
	[200]	0.0526	0.0536	0.0555
	$[21\bar{1}]$	0.0548	0.0537	0.0513
	$[22\bar{2}]$	0.0531	0.0494	0.0421
(113)	$[1\bar{1}0]$	0.0184	0.0138	0.0044
	$[12\bar{1}]$	0.0397	0.0413	0.0443
	$[03\bar{1}]$	0.0371	0.0368	0.0361

Table 2 gives the energy of kinks located in the more close packed ledges, in ε_c units. The energies are again not too different for the three potentials used and decrease as the atomic density in the ledge decreases.

TABLE 2 — Kink energies (ε_c units)

Ledge	Kink energy × 10		
	6 | 9	6 | 12	9 | 12
[011]	0.5447	0.6101	0.7409
[002]	0.1980	0.1665	0.1034
[112]	0.0683	0.0520	0.0195
[013]	0.0161	0.0114	0.0021
[222]	0.0095	0.0066	0.0010

Surface energies, γ, including terraces energies, γ_T, were calculated in the preceding paper [7]; they are shown in Table 2 of that paper.

The method that we use to calculate the lattice sums is quite accurate. It is described in the Appendix. For example, when the number of terms in the direct sums is increased by changing M from 10 to 15 (respectively $\sim 10^3$ and $\sim 15^3$ terms in the direct sums), the resulting relative change in ε_L is at most 10^{-3} for the 6 | 9 and 6 | 12 potentials and at most 10^{-4} for the 9 | 12 potential. A similar precision can be obtained for ε_K and γ_T (cf. ref. 7).

5.2 — *Applicability of the TLK Decomposition*

From a purely geometrical point of view, the TLK decomposition can be applied to any orientation of the surface and for any choice of the terraces and ledges. However, the surface energy calculated from eq. 8 using the energies of "pure" terraces and ledges of the same crystallography as that of the actual terraces and ledges, may deviate more or less from the true surface energy.

This is because, as the ledges become closer or the kink spacing decreases, the actual contribution of ledges and kinks to the surface energy will change, since they will interact with each other.

A first method for assessing the accuracy of the TLK decomposition is to compare the actual surface energies (see ref. 7) with those calculated by the TLK equation (eq. 8). Examples are given in Table 3 for planes vicinal to (002) and containing $[1\bar{1}0]$ or [200] ledges. The TLK values are calculated from eq. 8 using the energy contributions of ledges and kinks given in Tables 1 and 2 and the values of γ_T obtained in the preceding paper for (002). The correct values are written in italic; they are always larger than the TLK values. The agreement is excellent, even for planes deviating as much as ~25° from (002), for which the ledge separation is of the order of r_0.

TABLE 3 — Surface energies by TLK and by direct sum of planes with (002) terraces

Plane	Surface energies (ε_c / r_0^2 units) *					
	6 | 9		6 | 12		9 | 12	
113[a]	0.5115	*0.5172*	0.4678	*0.4717*	0.3803	*0.3805*
024[b]	0.5163	*0.5238*	0.4758	*0.4811*	0.3951	*0.3955*
115[a]	0.5166	*0.5176*	0.4710	*0.4717*	0.3799	*0.3799*
2 2 50[a]	0.5016	*0.5025*	0.4556	*0.4563*	0.3635	*0.3640*
2 2 100[a]	0.4979	*0.4980*	0.4520	*0.4520*	0.3601	*0.3601*
0 2 40[b]	0.5015	*0.5016*	0.4558	*0.4559*	0.3644	*0.3644*
0 2 100[b]	0.4971	*0.4971*	0.4513	*0.4513*	0.3597	*0.3597*
2 4 50[a]	0.5069	*0.5069*	0.4611	*0.4611*	0.3694	*0.3694*
4 6 50[a]	0.5122	*0.5123*	0.4664	*0.4665*	0.3747	*0.3747*
2 6 50[b]	0.5113	*0.5115*	0.4658	*0.4659*	0.3747	*0.3747*
4 6 20[a]	0.5202	*0.5231*	0.4760	*0.4779*	0.3874	*0.3875*

* The values in italic were obtained by direct sum.

a – $[1\bar{1}0]$ ledges; b – [200] ledges.

Table 4 refers to the errors in different TLK decompositions of the (6 8 10) plane, which makes similar angles with (002), (022) and (111). The smallest error among the various decompositions is always smaller than 1 %. Of course better descriptions, leading to smaller errors, would be possible for the (6 8 10) plane, including one in terms of (6 8 10) terraces for which the error would be zero.

TABLE 4 — Effect of the TLK decomposition on calculated surface energy of (6 8 10) plane

Terrace	Ledge	Θ_T (degrees)	Θ_L (degrees)	γ (ε_c / r_0^2 units)		
				6 | 9	6 | 12	9 | 12
(111)	$[1\bar{1}0]$	28.61	7.59	0.5139	0.4712	0.3856
(002)	$[1\bar{1}0]$	26.57	8.13	0.5143	0.4715	0.3859
(022)	[200]	27.69	35.26	0.5058	0.4652	0.3839
(022)	$[21\bar{1}]$	27.69	0	0.5054	0.4649	0.3839
(6 8 10)*	—	0	—	*0.5222*	*0.4769*	*0.3862*

* Direct sum.

An alternative method of showing the accuracy of the TLK values consists of plotting the correct surface energies of a family of planes containing (only) ledges of a given type and terraces of a given type, as a function of the angle between the plane and the terraces, Θ_T. From eq. 8 (with $\Theta_L = 0$)

$$\frac{\gamma}{\cos \Theta_T} = \gamma_T + \frac{\varepsilon_L}{h_L} \operatorname{tg} \Theta_T \tag{23}$$

Fig. 3a shows a plot $\gamma/\cos \Theta_T$ as a function of $\operatorname{tg} \Theta_T$ for planes vicinal to (002) and containing [110] ledges. Similarly, Fig. 3b applies to (002) terraces and [200] ledges. The curves are very nearly linear, deviating from linearity only at large angles. For (113) with $\Theta_T \simeq 25°$, the difference between the two terms of eq. 23 is at most 1 % (for the 6 | 9 potential).

A direct calculation of the error in the TLK equation is also possible. The method consists of comparing the correct eq. 12 with the TLK equation (eq. 8), in which the energies γ_T, ε_L, ε_K are calculated from eqs. 13-15. Consider, for example, the terrace term in the two equations. The difference results from the fact that in the TLK equation the atoms that enter in the lattice sum are those with $\mathbf{n} \cdot \mathbf{T} > 0$, whereas in the correct equation all atoms with $\mathbf{n} \cdot \mathbf{P} > 0$ are considered. The following result for the difference between the two sums is easily obtained, noting that for any atom **n** there is an atom **-n** :

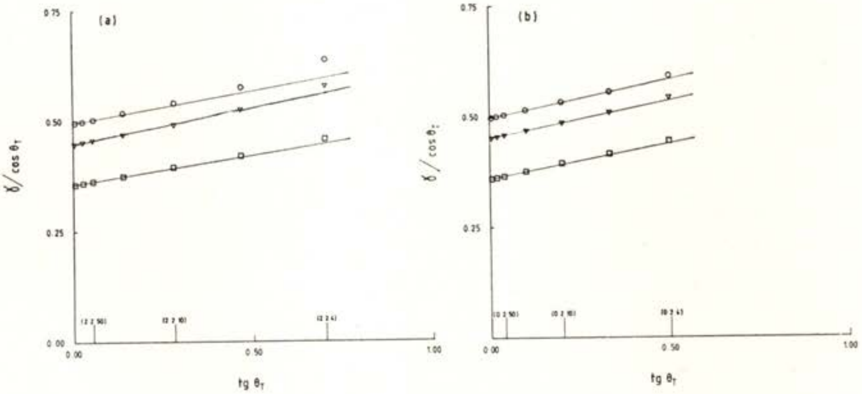

Fig. 3 — Variation of surface energy with orientation (Θ_T) for planes vicinal to (002): (a) in the $[1\bar{1}0]$ zone, $[1\bar{1}0]$ ledges; (b) in the [200] zone, [200] ledges. The surface energy is in $_c/r_0^2$ units. Potentials: ○ - 6 | 9; ▽ - 6 | 12; □ - 9| 12.

$$\sum_{\mathbf{n}\cdot\mathbf{T}>0} (\mathbf{n}\cdot\mathbf{T})\,\varepsilon(\mathrm{n}) - \sum_{\mathbf{n}\cdot\mathbf{P}>0} (\mathbf{n}\cdot\mathbf{P})\,\varepsilon(\mathrm{n}) = 2 \sum_{\substack{\mathbf{n}\cdot\mathbf{T}>0\\ \mathbf{n}\cdot\mathbf{P}<0}} (\mathbf{n}\cdot\mathbf{T})\,\varepsilon(\mathrm{n}) + \sum_{\substack{\mathbf{n}\cdot\mathbf{T}>0\\ \mathbf{n}\cdot\mathbf{P}=0}} (\mathbf{n}\cdot\mathbf{T})\,\varepsilon(\mathrm{n}) \qquad (24)$$

The first sum in the right-hand side is for all atoms in a wedge formed by the two planes **P** and **|** : this term has a factor 2. The other sum is for atoms in the plane **P** to one side of its intersection with **T**. The difference (24) is expected to be always negative thus explaining why the TLK surface energies are always smaller than those obtained by direct sum. The error in the other terms can be obtained by similar equations.

6 -- DISCUSSION

The fundamental equations derived in this paper are the equation for the surface energy in terms of contributions of the energies of terraces, ledges and kinks, and the lattice sums that give the specific energies of terraces, ledges and kinks.

As already noted, from a purely geometrical point of view, any TLK decomposition of a surface of arbitrary orientation is legitimate. From the point of view of energy, however, the TLK decomposition leads to an error which, in broad terms, increases as the spacing of ledges and the spacing of kinks decreases, and, on the other hand, as the atomic densities in terraces and ledges decrease.

The energy per unit area of a surface obtained from eq. 8 is always larger than the terrace specific energy. This points to the conclusion that the terraces should be chosen as planes for which pointed cusps occur in the γ-plots. These are in fact the more closed packed planes. In the f. c. c. crystals studied (Mye potentials) these planes are (111), (002) and (022). For similar reasons the ledges should be taken along directions, in each of these planes, corresponding to cusps in the ε_L-plot for that plane. Calculations show that these cusps occur in $<1\bar{1}0>$ and $<1\bar{1}2>$ directions in the (111) plane, in $<1\bar{1}0>$ and $<200>$ directions in the (002) planes and in $<01\bar{1}>$ and $<200>$ directions in (022) planes. Decompositions using such terraces and ledges are therefore those compatible with the observed cusps in the γ-and ε_L-plots.

A problem that can be raised concerns the range of applicability of the TLK decomposition using these low index terraces and ledges, and more generally any other set of terraces and ledges. The problem can be solved by finding the region in the stereographic triangle corresponding to planes for which the error in the TLK equation is smaller than a given amount, e. g. 1 %. Our calculations show that for the three more close packed terraces and for the two more close packed ledges in each of these planes, the error for the best TLK decomposition is at most ~1 %.

Clearly, the accuracy of the TLK decomposition of energy depends on the type of potential, particularly on its range. As the results (of Table 3, for example) show, the accuracy decreases as the ranges of the attractive and repulsive terms in the potential increase.

The analogy with the coincidence site lattice (c. s. l.) model of grain boundaries is worth a few comments. Formally any grain boundary can be described in terms of a reference c. s. l. boundary where a certain distribution of grain boundary dislocations is introduced. The good descriptions are those for which the dislocations are widely spaced, although a more sound test would be in terms of an energy criterion. For example, one could decompose the energy per unit area of any grain boundary as a sum of the energy of the c. s. l. boundary with terms due to the families of grain boundary dislocations [9]. The energy so calculated could be compared with that obtained directly, e. g. by computer calculations, and the error used as a test to the applicability of the model. Unfortunately, it is not easy to obtain the energy terms associated to the dislocations, and the range of applicability of the c. s. l. model has so far been evaluated simply from the spacing of the dislocations [e. g. 10].

APPENDIX – CALCULATION OF LATTICE SUMS FOR LEDGE AND KINK ENERGIES

The sum Δ_e (eq. 20c) is calculated term by term up to

$$n_1^2 + n_2^2 + n_3^2 \leqslant M^2$$

and the number, N, of atoms (terms) in the sum is counted. These atoms are within a half-circle in the plane (t), limited by a row [l] and centred in an atom 0_0 in that row (see Fig. 6 of preceding paper). The half-circle is in the half-plane C and its radius $R_0\, a/2$ is given by

$$\frac{\pi}{2} R_0^2 - \frac{t}{2\,l} R_0 = N\,t$$

since the area per atom in (t) is $(a^2/4)\,t$. The subtractive term corresponds to a rectangular region adjacent to the diameter through 0_0, of thickness equal to one-half of the interrow spacing, which is $(a/2)\cdot(t/l)$; no atom centres occur in this region. The rows $[\,l\,]$ in C, outside the semi-circle, are replaced by continuous layers of thickness equal to the interrow spacing and centred in each row, and with an atomic density equal to $4/(a^2 t)$. The region outside the half-circle is the difference between: (i) the area of the half-plane C outside the circle; (ii) a layer of thickness $(a/4)\,(t/l)$ adjacent to the diameter of the semi-circle and outside it.

The integrals that give the rest of the sum Δ_e are calculated in polar coordinates: ρ (in a/2 units), Θ. They have the form

$$\frac{1}{t}\,\frac{t}{l}\iint\frac{\rho\cos\Theta}{\rho^{e}}\,\rho\,d\Theta\,d\rho$$

since the number of rows m is

$$m=\rho\,\frac{t}{l}\,\cos\Theta$$

For the integral over region (i) defined above, the integration limits are: $\rho\,(R_0\,,\,\infty)$, $\Theta\,(0\,,\,\pi/2)$ leading to

$$\Delta'_e=[\,l\,(e-3)\,R_0^{e-3}\,]^{-1}$$

For the integral over region (ii), the integration limits are: $\rho\,(R_0\,,\,t/(2l\cos\Theta))$, $\Theta\,(\cos^{-1}t/(2lR_0)\,,\,\pi/2)$. Using the approximation $\cos\Theta\simeq\pi/2-\Theta$, we obtain

$$\Delta''_e=\frac{t^2}{l^3}\,\frac{1}{8\,(e-1)}\,\frac{1}{R_0^{e-1}}$$

The value of Δ_e is

$$\Delta_e=\sum_{n\leq M}\frac{m}{n}+\Delta'_e-\Delta''_e$$

The series ϕ_e (eq. 22) is calculated directly up to $k = k_0$. The rest of the sum is

$$\phi'_e = \int_{k_0+1/2}^{\infty} \frac{dk}{k^{e-1}} = [\,(e-2)\ (k_0 + 1/2)^{e-2}\,]^{-1}$$

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