SURFACE AND EVAPORATION ENERGIES OF MONOATOMIC CRYSTALS

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(Received 3 October 1985)

ABSTRACT — Using a corrected version of the method first developed by Shuttleworth, very precise calculations of surface energies for a large number of orientations of the surface in a monoatomic f. c. c. crystal have been undertaken. The effect of the exponent of the repulsive and attractive terms in the Mye-type potential function was studied; the exponents used were combinations of 12, 9 and 6. The surface energies were corrected for the relaxation of the more exposed surface atoms to their equilibrium positions, using a method based on the TLK decomposition of the surface. The corrections never exceed 1 %. These calculations also allow the determination of (relaxed) evaporation energies of surface atoms, particularly atoms in surface terraces, ledges and kink sites and of ad-atoms. The energies (measured in terms of the cohesive energy) are little affected by the potentials studied.

1 — INTRODUCTION

In this paper we report on results of computer calculations of surface energies and evaporation energies, with emphasis on the anisotropy of these quantities and on the effect of the interatomic potential. The surface energies are calculated by the method first used by Shuttleworth [1], with a correction in the determination of the rests of the lattice sums, for a wide range of orientations of the surface. A pairwise interaction between the atoms is assumed, with a potential energy $\varepsilon(\rho)$. The actual calculations were made for f. c. c. crystals with Mye potentials $6 | 9$, $6 | 12$, and $9 | 12$. All surface and evaporation energies were corrected for the relaxation of the more exposed surface atoms.

Similar calculations of surface energies for a wide range of orientations were undertaken by Nicholas [2] using Mye and Morse potentials, but he did not consider the correction due to relaxation. Nicholas' calculations extend previous work [3] on the anisotropy of the surface energy of cubic crystals, based on the broken-bond model. Although the results of Nicholas [2] were obtained for various potentials, no general conclusions were drawn on the effects of the potential range on the anisotropy of surface energy. These effects were considered by Drechsler and Nicholas [4] in relation to the equilibrium shapes of crystals, but again with no correction for surface relaxation.

The use of pairwise potentials for calculating the energies of surfaces and other crystal defects can of course be criticized (e. g. [5]), in special because of the difficulty of developing good potentials (particularly for metals, e. g. [6]), but is still the more efficient method of studying the structure and properties of crystal defects. Linford and Mitchell [7] introduced interplanar potentials, instead of pairwise interatomic potentials, to calculate surface energies, but their method is of restricted application. Finally, a few attempts have been made to calculate surface free energies (e. g. [8], [9]) and predict the effect of temperature on the surface tension.

2 – LATTICE SUMS FOR SURFACE ENERGY

Consider a crystal with one atom per lattice point, in which the atoms interact by a pairwise potential $\varepsilon(\rho)$, where ρ is the distance between the two atoms. A suitable vector basis $(\mathbf{e}_1\,\mathbf{e}_2\,\mathbf{e}_3)$ is chosen in the crystal. The relative positions of the atoms are defined by vectors of the type

$$\mathbf{n} = \sum_i n_i\,\mathbf{e}_i \qquad (1)$$

The permissible sets n_i have to be identified beforehand, for example, by relating the $\mathbf{e}_i$ to a lattice basis (if the $\mathbf{e}_i$ are a lattice vector basis, the n_i can take all integral values). The plane of the surface is defined by the Miller indices $(p) = (p_1\,p_2\,p_3)$ relative to the vector basis chosen. The (unrelaxed) surface energy $\gamma(p)$ is calculated from the potential energy, E, of interaction between two half-crystals, C and C′, separated by a plane (p), per unit area of this plane (Fig. 1). When relaxation

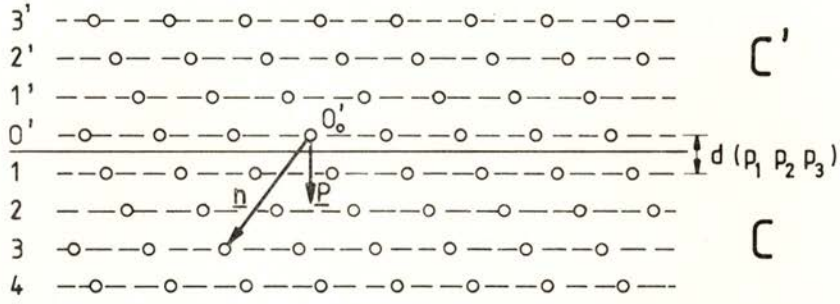


Fig. 1 — A crystal is divided into two half-crystals, C and C′, by a plane ($p_1\,p_2\,p_3$) of unit normal **P** and interplanar spacing d. When C and C′ are separated, two (identical) surfaces are created.

of the atomic positions is neglected, the surface energy is simply given by

$$\gamma = -E/2 \tag{2}$$

This follows directly from an energy balance and from the definition of surface energy as an excess energy, per unit area, relative to the perfect crystal.

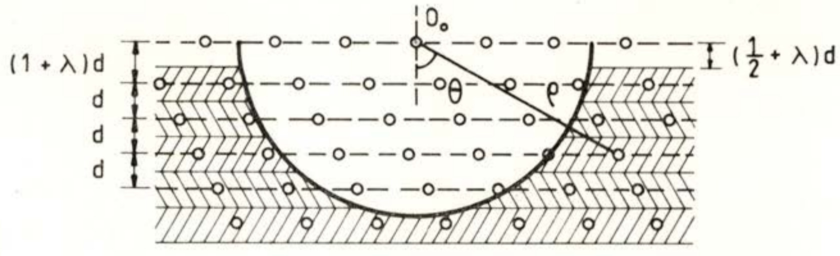


Fig. 2 — The topmost plane relaxes to a distance $(1+\lambda)$ d. The dashed region is treated as a continuum for calculating the rest of the sums D_e (see Appendix).

The atoms in the surface region will relax to new equilibrium positions, and this reduces the surface energy calculated from eq. (2). Consider first the relaxation of the atoms in the topmost plane (Fig. 2). We assume that this relaxation occurs exclusively along the normal to the plane. The corresponding correction to the surface energy is obtained as follows (cf. ref. [1]). Let $E^*(\lambda)$ be the potential energy, per unit area of the topmost plane, in the field of the other planes, λ being a measure of the relaxation of that plane ($\lambda = 0$ for zero relaxation). The atoms are assumed to keep the same positions as in the perfect crystal, except, of course, for the change in the distance of the top plane to the following plane. The value, λ_e, of λ that minimizes E^* is calculated. If E^*_e is the corresponding energy and E^*_0 is the energy for $\lambda = 0$, the corrected surface energy γ_c is

$$\gamma_c = \gamma + E^*_e - E^*_0 \tag{3}$$

The energies per atom will be indicated by ε's and the energy correction per atom by $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon^*_e - \varepsilon^*_0$).

In the calculation of E we use a generalized version of the method of Shuttleworth, with corrections in his procedure for calculating the lattice sums. In this method, the number of pairs of interacting atomic planes (p), one in half-crystal C, the other in C′, is the relevant quantity.

Taking for origin an atom position $0'_0$ in the plane of order $0'$ of C′, adjacent to the surface (Fig. 1), the positions of the atoms of crystal C are defined by all $\mathbf{n}$ such that

$$\frac{1}{d}(\mathbf{n}\cdot\mathbf{P}) = m \geqslant 1 \tag{4}$$

where d is the interplanar spacing and $\mathbf{P}$ is the unit normal to the surface plane. The number m is a (positive) integer that gives the order of the plane of C where the atom $\mathbf{n}$ is located (Fig. 1). For each $\mathbf{n}$, the number of pairs of planes, one in C the other in C′, with a spacing equal to m d, is precisely m. The potential energy of C′ in the field of C, per atom in the plane (p), can then be calculated from the potential energy $\varepsilon(\mathbf{n})$ of an atom in the plane 0′, provided this energy is multiplied by m and then summed for all $\mathbf{n}$ satisfying eq. (4). Finally, if v is the volume per atom, the area per atom in the plane (p) is v/d and the unrelaxed surface energy is

$$\gamma = -\frac{d}{2v}\sum_{\mathbf{n}} m\ \varepsilon(n)\,; \qquad m = \frac{1}{d}(\mathbf{n}\cdot\mathbf{P}) \geqslant 1 \tag{5}$$

which can be written as

$$\gamma(\mathbf{P}) = -\frac{1}{2v}\sum_{\mathbf{n}}(\mathbf{n}\cdot\mathbf{P})\ \varepsilon(n)\,; \qquad \mathbf{n}\cdot\mathbf{P} > 0 \tag{6}$$

This form of $\gamma(\mathbf{P})$ was first presented by Herring [10] and used by Nicholas [2] in his calculations.

3 – CORRECTION TO SURFACE ENERGY

We now turn to the correcting terms E* due to relaxation of the top plane from its unrelaxed position at a distance d from the following plane (Fig. 2). The relaxed distance is $(1+\lambda)\,d$, equivalent to a vector displacement $(-\lambda d\mathbf{P})$. The potential energy of the top plane, per unit area, is

$$E^*(\mathbf{P};\lambda) = \frac{d}{v}\sum_{\mathbf{n}}\varepsilon(|\mathbf{n}+\lambda\, d\mathbf{P}|) = \frac{d}{v}\varepsilon^*(\lambda)\,; \qquad \mathbf{n}\cdot\mathbf{P} > 0\,. \tag{7}$$

The values $E^*_0(\lambda=0)$ and $E^*_e(\lambda_e)$ at the minimum have to be determined to evaluate the correction to the surface energy (eq. 3) due to relaxation of the atoms in the top plane.

Except for the lower index planes, the relaxation of the atoms in planes following the topmost plane may give a non-negligible contribution to the correction. The method that we shall use to determine the correction to the surface energy in these cases is based on a description [11] of the surface in terms of terraces, ledges and kinks (TLK), such that the terraces and ledges are atomically compact, and the distances between ledges and between kinks are large compared to the interatomic spacing, as in the low atomic density surface of the two-dimensional crystal of Fig. 3.

In the companion paper we derive an equation (eq. 8 in ref. 11) for γ in terms of the contributions of terraces, ledges and kinks. From this equation we obtain for the correction $\Delta\gamma$ to the

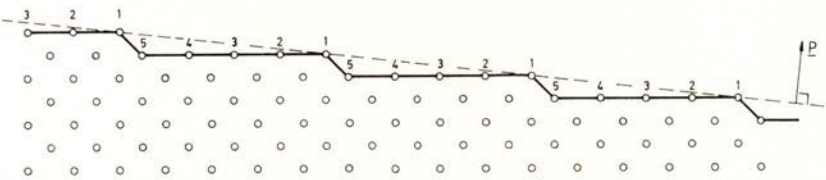


Fig. 3 — A two-dimensional crystal surface of orientation corresponding to the dashed line, showing terraces and ledges.

surface energy of a plane, with a particular decomposition TLK, the following result:

$$\Delta\gamma = \Delta\varepsilon_T \frac{d_T}{v} \cos\Theta_T + \frac{\Delta\varepsilon_L}{i_L\, d_T} \sin\Theta_T \cos\Theta_L + \frac{i_L}{v} \Delta\varepsilon_K \sin\Theta_T \sin\Theta_L \tag{8}$$

where $\Delta\varepsilon_T$, $\Delta\varepsilon_L$ and $\Delta\varepsilon_K$, respectively, are the corrections, per atom, for atoms in terraces, ledges and kink sites; d_T is the interplanar spacing of terraces, i_L the identity distance along ledges and v the volume per atom; Θ_T is the angle between the surface plane and the terraces and Θ_L the angle between the intersection of these planes with the direction of the ledges.

The total correction is then calculated by summing the corrections due to atoms in terraces, in ledges and in kinks. The latter is calculated from the correction for the topmost plane under consideration. The correction due to the terraces is directly obtained from the calculated $\varepsilon_e^* - \varepsilon_0^*$ for the plane of the terraces. Finally, the correction due to the ledges is obtained from that for a vicinal surface plane containing the same terraces and ledges (but no kinks) as the plane under consideration. In this method for obtaining the correction to the surface energy it is assumed that all atoms in terraces (e. g. atoms 2-5 in Fig. 3) and all atoms in ledges are equivalent. This is not strictly true: for example, the atoms in terraces near a ledge (e. g. atoms 2 or 5 in Fig. 3) are not in positions equivalent to those in terraces far from ledges (atoms 3 and 4). The error in the calculated corrections should then decrease as the width of terraces and the inter-kink distance increases.

4 – LATTICE SUMS FOR EVAPORATION ENERGIES

The evaporation energy is the absolute value of the potential energy of a surface atom in the field of all other atoms. For an atom in the topmost plane, the (corrected) evaporation energy is given by

$$\varepsilon_{ev} = - (\varepsilon_e^* + \varepsilon_p^*) \tag{9}$$

where ε_e^* is the contribution of planes below the top plane and ε_p^* is the potential energy due to the other atoms in the top plane. ε_e^* is calculated as described above (eq. 7) and ε_p^* is obtained from

$$\varepsilon_p^* = \sum_{\mathbf{n}} \varepsilon (n) ; \; \mathbf{n} \cdot \mathbf{P} = 0 ; \; \mathbf{n} \neq 0 \tag{10}$$

Evaporation energies of atoms in the second and following planes may de comparable to ε_{ev} in the case of high index planes. By considering a TLK description of the surface, the evaporation energies of other surface atoms (in terraces and in ledges) can be obtained; the evaporation energy for the topmost plane corresponds to the kink site atoms (ledge atoms, if the surface has no kink sites).

5 – APPLICATION TO F. C. C. CRYSTALS

We take three orthonormal vectors ($\mathbf{e}_1 \, \mathbf{e}_2 \, \mathbf{e}_3$) along the edges of the cube cell ($|\mathbf{e}_i| = 1$). If a is the lattice parameter, the general form of $\mathbf{n}$ is

$$\mathbf{n} = \frac{a}{2} \sum_i n_i \, \mathbf{e}_i \quad \text{with} \quad \sum_i n_i = \text{even} \tag{11}$$

the n_i being integers such that their sum is even. The Miller indices ($p_1\, p_2\, p_3$) will be taken as all odd (and coprime) or all even (g. c. d. = 2); then

$$d = \frac{a}{p} \quad ; \quad p^2 = \sum_i p_i^2 \ ; \quad \mathbf{P} = \frac{1}{p} \sum_i p_i\, \mathbf{e}_i \tag{12}$$

The interatomic distance in the crystal is $r_0 = a/\sqrt{2}$ and the volume per atom is $a^3/4$. The $e \mid e'$ Mye potential (namely $6 \mid 9$, $6 \mid 12$ and $9 \mid 12$, see Fig. 4) will be used

$$\varepsilon(\rho) = \varepsilon_0 \left[\left(\frac{\sigma}{\rho}\right)^{e'} - \left(\frac{\sigma}{\rho}\right)^{e} \right] ; \ e' > e \tag{13}$$

where ε_0 and σ are constants that can be related respectively to the cohesive energy per atom, ε_c, and to the equilibrium separation, r_0, in the crystal, by imposing that the potential energy of an atom is a minimum at the equilibrium separation. Table 1 gives

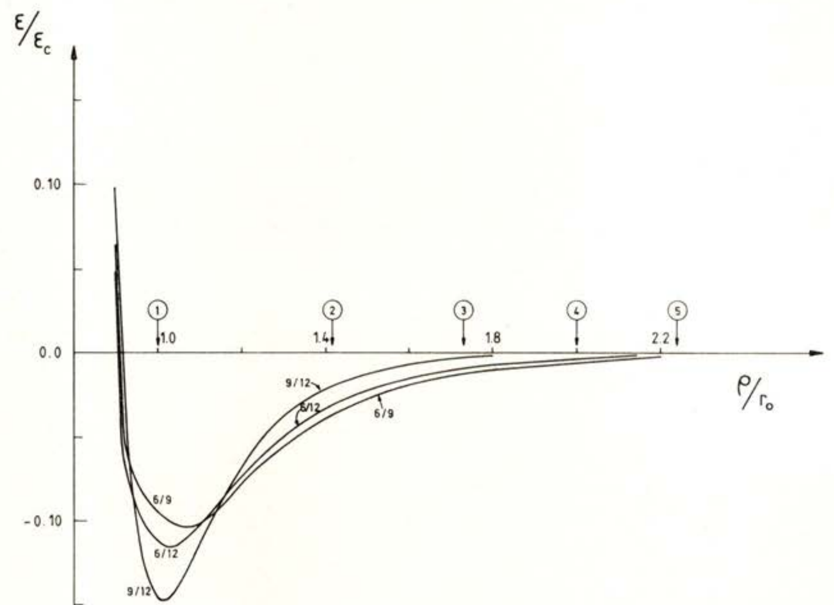


Fig. 4 — Plot of the potential functions $\varepsilon(\rho)$ used in the calculations. The energy is in ε_c units (cohesive energy in the crystal) and the distance in r_0 units (equilibrium 1st neighbour distance in the crystal). The distances to 2nd, 3rd, etc., neighbours are indicated.

values of σ/r_0 and $\varepsilon_0/\varepsilon_c$, obtained from very precise calculations of the lattice sums involved (cf. ref. [12]). Also indicated in Table 1 are the values of the equilibrium separation ρ_m and energy ε_m for an isolated pair of atoms. The fact that r_0/ρ_m is smaller than unity indicates that the near-neighbour interaction is repulsive for all potentials. This is in fact valid for any Mye potential [13].

TABLE 1 — Potential constants

	6 | 9 Potential	6 | 12 Potential	9 | 12 Potential
σ/r_o	0.91710	0.91729	0.91747
$\varepsilon_o/\varepsilon_c$	0.69769	0.46456	1.39026
r_o/ρ_m	0.95255	0.97123	0.99024
$-\varepsilon_m/\varepsilon_c$	0.10336	0.11614	0.14663

For the f. c. c. crystal with a potential e | e′, eq. 6 becomes

$$\gamma(\mathbf{P};\, e\,|\,e') = -\frac{\varepsilon_0}{r_0^2}\,(\sigma^{*e'}\, C_{e'} - \sigma^{*e}\, C_e) \tag{14}$$

where

$$\sigma^* = \sqrt{2}\;\sigma/r_0 \tag{15}$$

and

$$C_e = \sum_{\mathbf{n}} m'/\,n^e \tag{16a}$$

with

$$m' = \frac{1}{2p}\sum_i n_i\, p_i > 0\,;\; \sum_i n_i = \text{even}\,;\;\; n^2 = \sum_i n_i^2 \tag{16b}$$

The energy $E^*(\lambda)$ per unit area of the topmost plane, when its separation from the following plane is $(1+\lambda)\,d$, is obtained from eq. 7 noting that the displacement of the top plane is $-\lambda a p^{-2}\,(\sum_i p_i\, \mathbf{e}_i)$:

$$E^*(\lambda) = \frac{2}{p}\,\frac{\varepsilon_0}{r_0^2}\,(\sigma^{*e'}\, D_{e'} - \sigma^{*e}\, D_e) \tag{17}$$

where

$$D_e(\lambda) = \sum_{n} (n')^{-e} \tag{18a}$$

with

$$\frac{1}{2} \sum_i n_i\, p_i > 0\,;\ \sum_i n_i = \text{even}\,;\ n'^2 = \sum_i n_i'^2\,;\ n_i' = n_i + 2\lambda p^{-2}\, p_i \tag{18b}$$

Finally, the potential energy of an atom in a plane (p) due to the other atoms in the plane is given by

$$\varepsilon_p^* = \varepsilon_0\, (\sigma^{*e'}\, P_{e'} - \sigma^{*e}\, P_e) \tag{19}$$

where

$$P_e = \sum_{n \neq 0} n^{-e} \tag{20a}$$

with

$$\sum_i n_i\, p_i = 0\,;\ \sum_i n_i = \text{even}\,;\ n^2 = \sum_i n_i^2 \tag{20b}$$

6 – RESULTS AND DISCUSSION

All lattice sums, C_e, D_e and P_e were calculated by the methods described in the Appendix, with $M = 10$. The number of terms (atoms) in the direct sums was approximately 1000 for the series C and D. The rest of the sum C_6 for (002) is 2.3 % of the value obtained in the direct sum. This figure is 0.35 % for D_6 (with $\lambda = 0$). The figures for C_9 and D_9 are respectively 3.7×10^{-3} % and 1.2×10^{-3} % and for C_{12} and D_{12} they are about 5.10^{-6} %. The precision in the values of γ is quite good. For example, the value of γ for the (002) plane obtained with $M = 20$ is between $(0.3\text{-}5) \times 10^{-5}$ different from the value for $M = 10$ for the three potentials. All calculated values will be written with at most four or five digits, according to the cases.

The determination of the equilibrium relaxation λ_e of the top plane was found by calculating $E^*(\lambda)$ with increments of 0.001 in λ, starting at $\lambda = 0$.

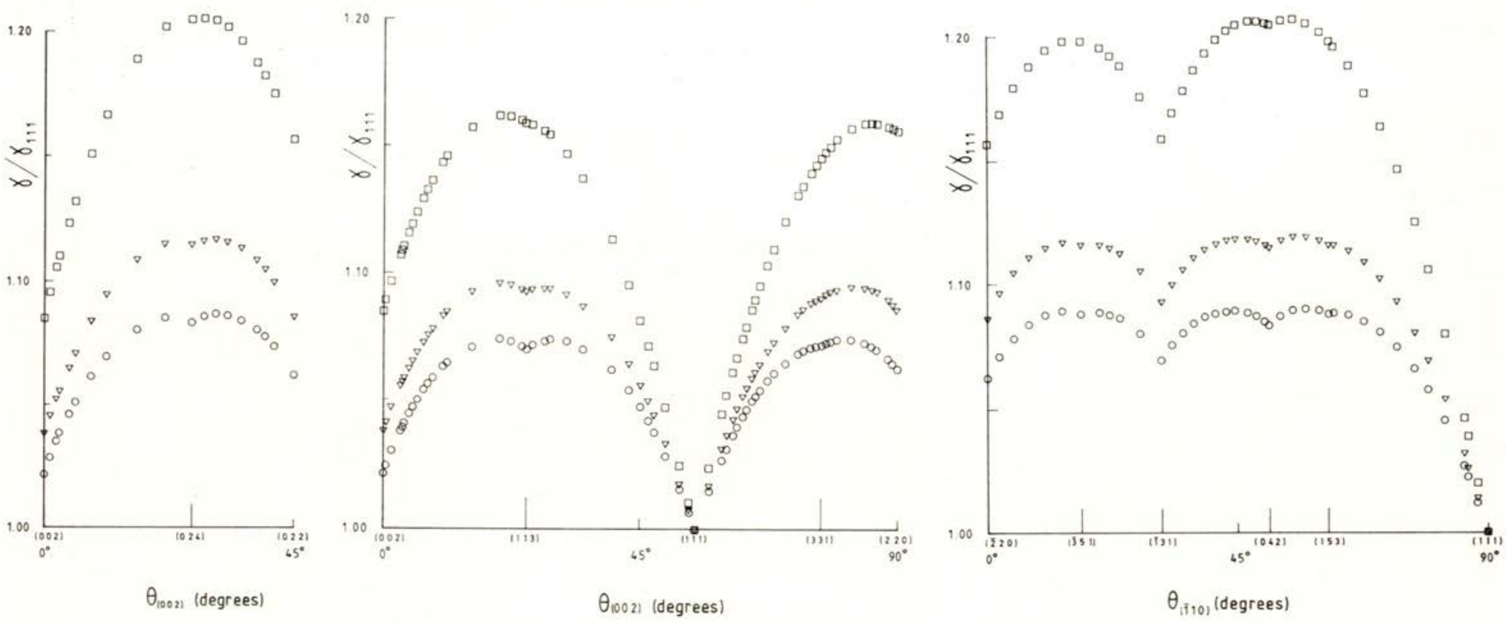
We shall consider separately the results for surface energies and for evaporation energies.

6a – SURFACE ENERGIES

Unrelaxed surface energies, γ, were calculated for a large number of planes and for the three potentials used (6 | 9, 6 | 12 and 9 | 12). In Table 2 are shown the values of γ for the more closely packed planes up to (135) and for a selected number of

TABLE 2 — Surface energies, γ (ε_c/r_o^2 units).

Plane	Potential		
	6 | 9	6 | 12	9 | 12
111	0.4831	0.4315	0.3283
002	0.4938	0.4480	0.3564
022	0.5137	0.4690	0.3798
113	0.5172	0.4717	0.3805
133	0.5181	0.4709	0.3763
024	0.5238	0.4811	0.3955
224	0.5172	0.4693	0.3735
115	0.5176	0.4717	0.3799
135	0.5259	0.4817	0.3933
100 100 102	0.4848	0.4333	0.3301
50 52 54	0.4890	0.4377	0.3350
500 502 520	0.4863	0.4348	0.3318
2 2 100	0.4980	0.4520	0.3601
2 100 100	0.5147	0.4699	0.3801
2 500 500	0.5139	0.4693	0.3798
0 2 40	0.5016	0.4559	0.3644
0 2 100	0.4971	0.4513	0.3597
0 30 38	0.5226	0.4784	0.3901
2 20 400	0.5017	0.4560	0.3645
1 15 19	0.5238	0.4794	0.3907
1 75 95	0.5229	0.4787	0.3903



(a) (b) (c)

Fig. 5 — Variation of uncorrected surface energies along various crystallographic zones: a) [200] zone; b) [$1\bar{1}0$] zone; c) [$11\bar{2}$] zone. Symbols for potentials: ○ - 6 | 9; ∇ - 6 | 12; □ - 9 | 12.

high index planes, most of which are vicinal to one of the lower index planes. From these data it is possible to calculate the contribution to the surface energy of edges and kinks in close packed planes. This will be discussed in detail in the companion paper. The γ values are expressed in units of ε_c/r_0^2, where ε_c is the cohesive energy per atom and r_0 is the interatomic distance. The values for the 6 | 12 potential are in excelent agreement with those that can be found in the work of Nicholas [2], but differ from those of Shuttleworth [1]. The 6 | 9 values are about 10 % larger than the 6 | 12 values and these are ~25 % larger than the 9 | 12 values, for the same surface planes. The data is conveniently displayed in γ-plots for individual zones, as shown in Figs. 5a-c respectively for the <100>, <1$\bar{1}$0> and <11$\bar{2}$> zones. The cusps at the lower index planes are clearly seen.

The fact that the relative values of γ for the three potentials are fairly independent of the surface orientation, suggests that if the γ values are expressed in another unit, characteristic of each potential, it might be possible to obtain values of γ fairly independent of the potential. Various attempts were made in this direction, using the data of Table 1, but without success. The energy depends on the interaction of a large number of atoms and it is not possible to write simple relations between the surface energy and properties of the interatomic potential.

The surface energy is least for (111) for all potentials. The largest γ found was for the plane (3 13 25) for the 6 | 9 and 6 | 12 potentials and for (1 7 13) for the 9 | 12 potential. These results on the maximum contrast with the conclusions drawn from a broken first-neighbour bond model [3, 4], according to which the maximum γ occurs for (024). The anisotropy, measured by the ratio of the two extreme γ's, is 1.207, 1.120 and 1.091 respectively for the 9 | 12, 6 | 12 and 6 | 9 potentials, in agreement with the general effect of the potential range on the anisotropy of γ [4].

Table 3 gives the equilibrium potential energy ε_e^* of an atom in a topmost plane, in the field of the atoms below that plane. The unit is ε_c. The values for each potential vary by a factor of ~1.6 between the maximum and minimum; they are slightly larger for the 6 | 9 potential and smaller for the 9 | 12 potential.

The calculated relaxations, expressed in r_0 units, vary between 1.2 and 2.5 % for the 6 | 9 potential, between 0.7 and 1.5 % for the 6 | 12 potential and between 0.2 and 0.5 % for the 9 | 12 potential. The smallest values are for (111), while (024) has values of the relaxation close to the maximum (which in fact occurs for a high index plane).

The corrections to the surface energy due to relaxation of the top plane, i. e. the values of $\varepsilon_0^* - \varepsilon_e^*$, are also indicated in Table 3. The values are per atom, in $_{\mathrm{c}}$ units.

TABLE 3 — Energy of atoms in top plane, ε_e^*, and energy correction, $\varepsilon_e^* - \varepsilon_o^*$, per atom

Plane	$-\varepsilon_e^*$ (ε_c units)			$\varepsilon_o^* - \varepsilon_e^*$ (ε_c units) $\times 10^2$		
	6 | 9	6 | 12	9 | 12	6 | 9	6 | 12	9 | 12
111	0.6490	0.6143	0.5468	0.2672	0.1177	0.0086
002	0.7115	0.6940	0.6636	0.7535	0.3731	0.0634
022	0.8358	0.8302	0.8247	0.8843	0.4201	0.0602
113	0.8713	0.8607	0.8448	0.8104	0.3818	0.0515
133	0.8956	0.8797	0.8523	0.6892	0.3197	0.0391
024	0.9427	0.9501	0.9722	1.1403	0.5435	0.0822
224	0.8994	0.8825	0.8529	0.6417	0.2960	0.0354
115	0.9027	0.8845	0.8533	0.8329	0.3990	0.0587
135	0.9781	0.9807	0.9923	0.9872	0.4623	0.0634
100 100 102	0.9014	0.8846	0.8531	0.2875	0.1251	0.0094
50 52 54	0.9898	0.9912	0.9962	0.3234	0.1404	0.0115
500 502 520	1.0030	1.0013	1.0001	0.3030	0.1311	0.0100
2 2 100	0.9063	0.8872	0.8537	0.7756	0.3810	0.0633
2 100 100	0.9072	0.8875	0.8536	0.8681	0.4128	0.0589
2 500 500	0.9073	0.8875	0.8536	0.8760	0.4170	0.0599
0 2 40	0.9697	0.9714	0.9801	0.8398	0.4078	0.0668
0 2 100	0.9694	0.9713	0.9800	0.8072	0.3928	0.0650
0 30 38	0.9715	0.9721	0.9800	1.0140	0.4799	0.0691
2 20 400	1.0083	1.0040	1.0007	0.8331	0.4051	0.0660
1 15 19	1.0091	1.0042	1.0006	0.9870	0.4662	0.0657
1 75 95	1.0100	1.0047	1.0007	1.0043	0.4760	0.0680

TABLE 4 — Surface energy corrections using TLK decomposition (ε_c/r_o^2 units)

Plane	Terrace	Ledge	Vicinal plane for $\Delta\varepsilon_L$	$\Delta\gamma$ ($\times 10^2$)		
				6 | 9	6 | 12	9 | 12
111	111	—		0.3085	0.1359	0.0099
002	002	—		0.7535	0.3731	0.0634
022	022	—		0.6253	0.2971	0.0426
113	113	—		0.4887	0.2302	0.0311
113	002	$1\bar{1}0$		1.1703	0.5677	0.0884
113	111	$1\bar{1}0$		0.7572	0.3485	0.0397
133	022	$01\bar{1}$		0.9248	0.4358	0.0594
133	111	$01\bar{1}$		0.6023	0.2727	0.0271
024	002	200		1.1839	0.5768	0.0935
024	022	200		1.1032	0.5249	0.0771
224	002	$1\bar{1}0$		1.1392	0.5463	0.0807
224	111	$1\bar{1}0$		0.5529	0.2490	0.0238
115	002	$1\bar{1}0$		1.0456	0.5126	0.0836
135	111	$1\bar{2}1$		0.6047	0.2757	0.0302
135	022	211		0.9316	0.4403	0.0621
100 100 102	111	$1\bar{1}0$		0.3118	0.1373	0.0100
50 52 54	111	$1\bar{2}1$		0.3156	0.1390	0.0102
500 502 520	111	$1\bar{1}0$	100 100 102	0.3154	0.1389	0.0102
2 2 100	002	$1\bar{1}0$		0.7842	0.3882	0.0659
2 100 100	022	$01\bar{1}$		0.6498	0.3087	0.0442
2 500 500	022	$01\bar{1}$		0.6302	0.2994	0.0429
0 2 40	002	200		0.7945	0.3930	0.0667
0 2 100	002	200		0.7695	0.3809	0.0647
0 30 38	022	200		0.7886	0.3743	0.0537
2 20 400	002	200	0 2 40	0.8028	0.3970	0.0673
1 15 19	022	$21\bar{1}$	1 3 5	0.8378	0.3969	0.0564
1 15 19	022	200	0 30 38	0.8694	0.4125	0.0591
1 75 95	022	200	0 30 38	0.8051	0.3822	0.0548

The smallest correction per atom is for (111) and the largest is for (024); these corrections differ by a factor of ~4 for the $6 \mid e'$ potentials and by a factor of ~8 for the $9 \mid 12$ potential. The correction is very small for the $9 \mid 12$ potential and largest for the $6 \mid 9$ potential, but even for this potential does not exceed ~1 %.

Corrected surface energies were obtained with the values of Table 3, using eq. 8 and an appropriate TLK description of the

TABLE 5 — Corrected surface energies, γ_c (TLK corrections)

Plane	$\gamma_c\,(\varepsilon_c/r_o^2$ units)		
	$6 \mid 9$	$6 \mid 12$	$9 \mid 12$
111	0.4800	0.4301	0.3282
002	0.4863	0.4443	0.3558
022	0.5074	0.4660	0.3794
113	0.5096	0.4682	0.3801
133	0.5121	0.4682	0.3760
024	0.5128	0.4759	0.3947
244	0.5117	0.4668	0.3733
115	0.5071	0.4666	0.3791
135	0.5199	0.4789	0.3930
100 100 102	0.4817	0.4319	0.3300
50 52 54	0.4858	0.4363	0.3349
500 502 520	0.4831	0.4334	0.3317
2 2 100	0.4902	0.4481	0.3594
2 100 100	0.5082	0.4668	0.3797
2 500 500	0.5076	0.4663	0.3794
0 2 40	0.4937	0.4520	0.3637
0 2 100	0.4894	0.4475	0.3591
0 30 38	0.5147	0.4747	0.3896
2 20 400	0.4937	0.4520	0.3638
1 15 19	0.5151	0.4753	0.3901
1 75 95	0.5148	0.4749	0.3898

surface. The terraces were chosen among (111), (002) and (022) and the ledges among the directions [011], [002] and [112]. For each decomposition, the correction to the surface energy is given in Table 4 in ε_c/r_0^2 units. When the plane has no kinks, $\Theta_L = 0$, the correction $\Delta\varepsilon_L$ is the value found in Table 3 for that plane. If there are kinks, $\Delta\varepsilon_L$ is taken from Table 3 for a plane (indicated in Table 4) vicinal to the surface plane and with a TLK decomposition with no kinks; $\Delta\varepsilon_K$ is then the correction per atom for the surface plane.

Also included in Table 4 are the corrections to the four most close packed planes, calculated directly from the correction per atom for these planes, given in Table 3.

The corrected energies are given in Table 5 for the planes listed in Table 4. For planes with two TLK decompositions in Table 4, the correction corresponding to the decomposition with more close packed terraces (or ledges, in the case of (1 15 19)) was used. It is apparent that the correction slightly reduces the anisotropy of the surface energy (reduction of 1.5 % for the 6|9 potential). It also reduces the increase of γ for a given deviation away from a close packed orientation.

6b – EVAPORATION ENERGIES

The calculated potential energies ε_p^* of an atom in a crystal plane due to the other atoms in the plane are indicated in Table 6, in ε_c units. The values for the high index planes such as (2 100 100), (0 2 100) and (50 52 54) are very nearly those contributed by atoms in the lattice row, parallel to <001>, <002> and <112>, respectively, where the reference atom is located. This is because in these planes, the rows indicated have inter-row spacings much larger than the repeat distance along the row. For similar reasons, the atoms in planes such as (1 75 95) are so far apart that the potential energy ε_p^* is negligible. Combining these results with the ε_e^* values of Table 3, corrected evaporation energies from the topmost planes can be calculated (eq. 8). The results are shown in Table 7.

As expected, the evaporation energy decreases as the compactness of the surface plane decreases, for the more close packed

TABLE 6 — Potential energy ε_p^*, per atom due to atoms in the same plane

Plane	$-\varepsilon_p^*$ (ε_c units)		
	6 | 9	6 | 12	9 | 12
111	0.7073	0.7737	0.9065
002	0.5919	0.6193	0.6741
022	0.3459	0.3479	0.3518
113	0.2734	0.2861	0.3114
133	0.2224	0.2470	0.2961
024	0.1374	0.1107	$0.5729.10^{-1}$
224	0.2140	0.2409	0.2948
115	0.2112	0.2390	0.2945
135	$0.6343.10^{-1}$	$0.4784.10^{-1}$	$0.1666.10^{-1}$
100 100 102	0.2029	0.2333	0.2940
50 52 54	$0.2671.10^{-1}$	$0.2040.10^{-1}$	$0.7790.10^{-2}$
2 2 100	0.2029	0.2333	0.2940
2 100 100	0.2029	0.2333	0.2940
2 500 500	0.2029	0.2333	0.2940
0 2 40	$0.7722.10^{-1}$	$0.6523.10^{-1}$	$0.4126.10^{-1}$
0 2 100	$0.7722.10^{-1}$	$0.6523.10^{-1}$	$0.4126.10^{-1}$
0 30 38	$0.7722.10^{-1}$	$0.6523.10^{-1}$	$0.4126.10^{-1}$
500 502 520	$0.1123.10^{-5}$	$0.7491.10^{-6}$	$0.1960.10^{-8}$
2 20 400	$0.2320.10^{-6}$	$0.1547.10^{-6}$	$0.1007.10^{-9}$
1 15 19	$0.1437.10^{-2}$	$0.9812.10^{-3}$	$0.6878.10^{-4}$
1 75 95	$0.2477.10^{-4}$	$0.1658.10^{-4}$	$0.1890.10^{-6}$

planes (from (111) to (135)). The (024) plane has a slightly lower value, which can be attributed to the low ε_p^* for this plane.

The evaporation energies for the following high index planes (from (100 100 102) to (0 30 38)) correspond to atoms which are located at atomic ledges separating low index terraces. The ledges are, depending on the cases, along <110>, <200> and

TABLE 7 — Evaporation energies, ε_{ev}

Plane	ε_{ev} (ε_c units)		
	6 | 9	6 | 12	9 | 12
111	1.3563	1.3880	1.4534
002	1.3035	1.3134	1.3377
022	1.1818	1.1781	1.1765
113	1.1448	1.1468	1.1563
133	1.1181	1.1267	1.1485
024	1.0800	1.0608	1.0295
224	1.1134	1.1234	1.1478
115	1.1139	1.1235	1.1479
135	1.0415	1.0285	1.0090
100 100 102	1.1043	1.1179	1.1471
50 52 54	1.0166	1.0116	1.0040
2 2 100	1.1092	1.1204	1.1476
2 100 100	1.1101	1.1208	1.1476
2 500 500	1.1102	1.1208	1.1476
0 2 40	1.0470	1.0367	1.0213
0 2 100	1.0467	1.0365	1.0213
0 3 38	1.0487	1.0374	1.0213
500 502 520	1.0030	1.0013	1.0001
2 20 400	1.0083	1.0040	1.0007
1 15 19	1.0105	1.0051	1.0007
1 75 95	1.0100	1.0047	1.0007

<112> directions (see Table 4). It is noticeable that the evaporation energies of such ledge atoms are fairly constant, i. e., nearly independent of the low index terrace associated with the ledge, and decrease as the atomic density in the ledge decreases.

The evaporation energies per atom in top planes which do not contain close packed rows (the last four planes in Table 7) are also fairly constant. They correspond to atoms at kink sites. It is interesting to note that the evaporation energies of such atoms can be as much as 1 % larger than the cohesive energy for the 9|6 potential.

It is apparent from the values of Table 7 that there is no systematic effect of the potential on the evaporation energies expressed in ε_c units. This contrasts with the marked effect on the γ values expressed in ε_c/r_0^2 units.

Finally, it is noted that the energies ε_e^* in Table 3 for the low index planes are the evaporation energies for isolated ad-atoms sitting on these planes. Such energies increase as the atomic density in the plane decreases.

APPENDIX — CALCULATION OF LATTICE SUMS

The sums C_e, D_e and P_e are calculated term by term up to a chosen value of $n = |\mathbf{n}|$:

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

and the number, N, of terms in the sum, is counted. The region within which these atoms are located is then determined (e. g. a hemisphere or a circle). The rest of the series is calculated assuming that the remainder of crystal C is replaced by a continuum with the appropriate atomic density.

The correct assignment of the volume where the N atoms are located is crucial, if precise results are wanted. Shuttleworth assumed that this volume, in the case of the series C_e, is a hemisphere in crystal C of radius $R_0\, a/2$, centred at atom $0'_0$ in the first plane $0'$ of C' (Fig. 6) and such that $(2\pi/3)\, R_0^3 = 2N$. Using this criterion we have obtained incoherent results: for example, the surface energy for (2 500 500) is smaller than that for (022). Since among the N atoms there are no atoms in the plane through $0'_0$, it is apparent that the volume in crystal C where the atoms are located is the volume of a hemisphere centred at $0'_0$, minus the volume of a layer adjacent to the plane through $0'_0$ and of thickness $d/2 = (a/2) \cdot (1/p)$ (see Fig. 6). This is consistent with the procedure that will be adopted to evaluate the rest of the series. Therefore the radius $R_0\,a/2$ of the sphere is given by

$$(2\pi/3)\ R_0^3 - \pi R_0^2\ (1/p) = 2N$$

The difference between the R_0 determined by this equation and by Shuttleworth's equation tends to zero as the interplanar distance $d \rightarrow 0$, but for lower index planes the differences are significative leading to changes of about 0.2 % in the surface energy of (002), with the $6\,|\,12$ potential. This results mostly from the change in C_6 which is the slowest convergent sum.

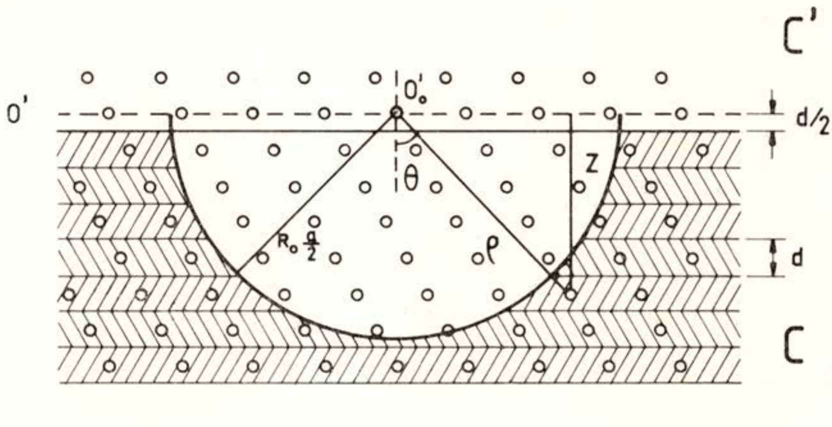


Fig. 6 — Illustration of the method used to obtain the rest of the lattice sums C_e (see Appendix). The half-crystal C is replaced by a continuum outside a hemisphere of radius $R_0\ a/2$.

The atomic planes (p) outside the hemisphere are replaced by continuous lamella of thickness d/2 centred in each plane (Fig. 6). The integration domain for the integrals that give the rest of the series is the difference between the following two regions: i) the volume below plane 0′ outside the hemisphere; ii) a lamella of thickness d/2 limited by that plane, outside the hemisphere. Shuttleworth wrongly assumed that region ii) was a lamella outside a cylinder of radius R_0.

Using spherical coordinates, (ρ , Θ , ϕ) and expressing all linear dimensions in units of a/2 (volume per atom = 2), we have (cf. eq. 16a)

$$m' = \rho \cos\Theta / d$$

and the integrals that have to be calculated are of the form

$$\iiint \rho^{3-e} \sin\Theta \cos\Theta \, d\rho \, d\Theta \, d\phi$$

For the integral over region (i) the integration limits are: $\phi (0 , 2\pi)$; $\Theta (0 , \pi/2)$; $\rho (R_0 , \infty)$, with the result

$$C'_e = \frac{\pi}{e-4} \frac{p}{4} \frac{1}{R_0^{e-4}}$$

For the integral over region (ii) the integration limits are: $\phi (0, 2\pi)$; $\rho (R_0 , \frac{1}{p \cos\Theta})$; $\Theta (\cos^{-1} \frac{1}{R_0 p} , \pi/2)$ with the result:

$$C''_e = \frac{\pi}{4p (e-2)} \frac{1}{R_0^{e-2}}$$

The series C_e is then calculated from

$$C_e = \sum_n \frac{m'}{n^e} + C'_e - C''_e \; ; \; n^2 = \sum_i n_i^2 \leqslant M^2$$

In the case of the series D_e the sum is calculated term by term up to

$$\Sigma \; n_i'^2 \leqslant M^2$$

The corresponding N atoms are within a hemisphere of radius $R_0 \, a/2$ centred at 0_0 with (Fig. 2).

$$(2\pi/3) \; R_0^3 - \pi R_0^2 \cdot (2\lambda + 1)/p = 2N$$

The second term in the left corresponds to a layer of thickness $d/2 + \lambda d$ where no atom centres lie. This integration volume is again the difference between: i) the half-space below plane 0 outside the hemisphere; ii) a lamella of thickness $(1/2 + \lambda)\, d = (1 + 2\lambda)/p \cdot a/2$ outside the hemisphere and adjacent to plane 0. The integrals for the rest of the sum D_e are

$$\iiint \rho^{2-e} \sin\Theta \; d\rho \; d\Theta \; d\phi$$

For the integral over region (i): $\phi\,(0, 2\pi)$; $\Theta\,(0, \pi/2)$, $\rho\,(R_0, \infty)$ with the result

$$D'_e = \frac{\pi}{e-3} \frac{1}{R_0^{e-3}}$$

For the integral over region (ii): $\phi\,(0,\ 2\pi)$; $\rho\,(R_0, \dfrac{1+2\lambda}{p \cos\Theta})$;

$\Theta\,(\cos^{-1} \dfrac{1+2\lambda}{p\,R_0}, \dfrac{\pi}{2})$ with the result

$$D''_e = \frac{2\pi}{p} \left(\frac{1}{2} + \lambda \right) \frac{1}{(e-2)\, R_0^{e-2}}$$

The series D_e is then calculated from

$$D_e = \sum_n \frac{1}{n'^e} + D'_e - D''_e \quad n'^2 = \sum_i n_i'^2 \leqslant M^2$$

Finally in the calculation of P_e the direct sum is determined for N atoms within a circle of radius $R_0\, a/2$ such that

$$\pi R_0^2 = Np$$

The atoms outside this circle are replaced by a continuum with atomic density $(p\, a^2/4)^{-1}$. The rest of the sum is

$$P'_e = \frac{1}{p} \int_{R_0}^{\infty} 2\pi \; \rho^{1-e} \; d\rho = \frac{2\pi}{p} \frac{1}{e-2} \frac{1}{R_0^{e-2}}$$

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