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Energetics of steps and kinks on Ag and Pt using equivalent crystal theory (ECT)

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Abstract

Using the equivalent crystal theory (ECT), we have calculated the energies of steps and kinks on vicinal {001} and {111} surfaces of Ag and Pt. We compare with some semiempirical calculations, particularly our recent embedded atom method (EAM) results, and with available experimental data, considering both trends and magnitudes: ECT values are roughly double those from EAM, and may well be more accurate. Like EAM, ECT incorrectly predicts an instability of Ag{110} towards missing row reconstruction.

1. Introduction

In recent years a surge in the study of surface phenomena has led to an interest in surface morphology. The goal is deeper understanding of such behavior as epitaxial growth, chemical reactivity of adsorbate molecules, and surface reactivity. Steps and kinks are the basic ingredients in the description of surface morphology. In general the symmetry of such systems is too low to allow for self-consistent total energy approaches (except for simple, light materials [1]). Thus, investigators eager to gain some understanding of the important energies have relied on semiempirical methods, most often the embedded atom method (EAM) [2–6], sometimes alternative related schemes [7]. While EAM has been impressively successful [6] in describing a wide variety of properties of late transition and noble metals, including many surface properties, a significant shortcoming is that the estimate of surface energies is considerably lower than found by local-density-approximation, total-energy calculations [8,9] and in experiments [10]. (While this problem in EAM has been linked to the neglect of presumably strong gradient corrections near surfaces [11], the deficiency may be more general: recent calculations have found EAM numbers to be about half those of density functional theory for stacking faults and for twin boundaries in Al [12].) Since step energies can at least crudely be approximated by a difference in surface energies (cf. the "awning" approximation

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discussed below), one is led to wonder whether the magnitudes of EAM calculations of step and kink energies [5,13,14] are also too small.

In recent years, a new semiempirical approach, equivalent crystal theory (ECT), has been formulated [8]. The surface energies in this approach are much closer to experimental and first-principles computational results [9]. In this paper we present a calculation of the principal step and kink energies of vicinal {001}, {111}, and {110} surfaces of Ag and Pt at temperature $T = 0$ using ECT. Our focus on energies contrasts with previous applications of ECT to vicinal surfaces, which emphasized relaxations [15].

In this short paper, we first give a utilitarian explanation of the ECT method, followed by some formal background on definitions of energies of steps and kinks. We then report and discuss our calculations and results, comparing with previous calculations and measurements.

2. ECT

In this section a brief operational description of the ECT method is given. Details of its derivation and the rationale behind its development are found in Refs. [8] and [15]. In ECT any deviation of a solid from its zero-temperature infinite-bulk structure occupying all of three-dimensional space is considered a defect. Thus, for example, even a perfect bulk-terminated surface of an fcc metal at $T = 0$ is considered a defect in a solid. If ε is defined as the total energy required to form a defect, then

$$\varepsilon = \sum_i \varepsilon_i, \tag{1}$$

where ε_i is the contribution to ε from the atom i close to the defect; the sum runs over all such atoms with non-zero contributions ε_i. In the ECT calculational scheme there exists for each of these atoms i an equivalent perfect single effective crystal filling all space at $T = 0$ such that the energy ε_i of atom i in the actual defect crystal is the same as in the equivalent perfect crystal. The equivalent crystal differs from a perfect defect-free crystal of the same substance only in that its lattice constant differs from the physical bulk value. The problem of finding ε_i, and hence ε, is reduced to finding for each atom i an effective equivalent single crystal and calculating the energy of the atom i in it. This is easier said than done: many-body terms contribute to the energy of each atom in real systems. Hence, ε_i is written as a sort of perturbation series of one-, two-, three- and four-body terms, each of which is obtained by considering a different effective perfect equivalent single crystal. In this approximation, ε_i takes the form:

$$\varepsilon_i = \Delta E \left(F^* [a_1^*(i)] + \sum_j F^* [a_2^*(i,j)] + \sum_{j,k} F^* [a_3^*(i,j,k)] + \sum_{j,k} F^* [a_4^*(i,j,k)] \right), \tag{2}$$

where

$$F^* [a^*] = 1 - (1 + a^*) \exp(-a^*). \tag{3}$$

The four different values of a_i^* for $i = 1, 2, 3$ and 4 are given by

$$a_i^* = (R_{ec,i} - r_{WSE}) / l, \tag{4}$$

where $R_{ec,i}$, $i = 1, 2, 3$ and 4, are the nearest-neighbor (nn) spacings in the effective equivalent perfect single crystals corresponding to the one-, two-, three-, and four-body terms of the ith atom,

respectively. In the discussion above and the one to follow, the parameters α, β, r_{WSE}, l, λ, p, ΔE, A_2, A_3, A_4 are all obtained from the only experimental input to the method, namely the three bulk elastic constants, the bulk cohesive energy, the bulk lattice constant, and the vacancy formation energy. $R_{ec,1}$ is obtained by solving numerically the transcendental equation which represents local atom density changes:

$$
N_1 R_{ec,1}^p \exp(-\alpha R_{ec,1}) + N_2 (c_2 R_{ec,1})^p \exp\left[-(\alpha + \lambda^{-1}) c_2 R_{ec,1}\right]
$$
$$
- \sum_{\text{defect}} R_j^p \exp\left[-\{\alpha + S(R_j)\} R_j\right] = 0 \tag{5}
$$

where the sum over the defect crystal is over all neighbors within second nearest neighbor (nnn) distance. R_j is the distance between atom i and a neighboring atom j, N_1 and N_2 are the number of nearest neighbors (nn) and next-nearest neighbors of the equivalent crystal, repectively. c_2 is the ratio of the nnn distance to the nn distance in the perfect solid, which for fcc metals is $\sqrt{2}$. $S(R_j)$ is a screening function given by:

$$
S(R) = \begin{cases} 0 & \text{if } R \le R_0 \\ (2\lambda)^{-1}\left[1 - \cos\{\pi(R - R_0)/(c_2 R_0 - R_0)\}\right] & \text{if } R_0 \le R \le c_2 R_0 \\ \lambda^{-1} & \text{if } c_2 R_0 \le R \end{cases} \tag{6}
$$

where R_0 is the nn distance in the perfect bulk solid. $R_{ec,2}$ is obtained by solving numerically the transcendental equation which represents nn bond length changes:

$$
N_1 R_{ec,2}^p \exp(-\alpha R_{ec,2}) - N_1 R_0^p \exp(-\alpha R_0)
$$
$$
+ A_2 R_0^p \sum_j (R_j - R_0) \exp\left[-\beta(R_j - R_0)\right] = 0. \tag{7}
$$

$R_{ec,3}$ is obtained by solving numerically the transcendental equation which represents changes in the nn bond angles:

$$
N_1 R_{ec,3}^p \exp(-\alpha R_{ec,3}) - N_1 R_0^p \exp(-\alpha R_0)
$$
$$
+ A_3 R_0^p \exp\left[-\alpha(R_j - 2R_0 + R_k)\right] \sin|\theta_{jk} - \theta| = 0. \tag{8}
$$

Here θ_{jk} is the angle between the nn position vector $\mathbf{R}_j$ of atom j with respect to atom i and the position vector $\mathbf{R}_k$ of atom k with respect to atom i in the defect crystal. θ is the equilibrium value of this angle in the bulk perfect crystal.

$R_{ec,4}$ is likewise obtained from the transcendental equation which represents changes in the body diagonal of the fcc unit cell:

$$
N_1 R_{ec,4}^p \exp(-\alpha R_{ec,4}) - N_1 R_0^p \exp(-\alpha R_0)
$$
$$
+ A_4 R_0^p (|d_p - d_q|/d) \exp\left[-\alpha(R_j + R_k + R_l + R_m - 4R_0)\right] = 0, \tag{9}
$$

where d is the face diagonal of the undistorted cube, and d_p and d_q are the face diagonals in the defect crystal.

3. Steps and kinks

3.1. Formal background

In this section some formal definitions of step and kink energies are recapitulated. For vicinal surfaces, tilted by an angle ϕ from a low index face, the surface energy per unit *projected* area $f(\phi, T)$ (the projection being onto the low-index plane of the terraces) can be expanded with respect to the average density of steps [16,17] as

$$f(\phi, T) = f(0, T) + \beta(T)|\tan\phi|/h + g(T)|\tan\phi|^3. \tag{10}$$

The first term $f(0, T)$ is the surface free energy per unit area of the terrace plane. The average density of steps (i.e. the inverse of their mean separation) is $|\tan\phi|/h$, where h is the step height. $\beta(T)$ is the free energy *per unit length* of step formation at an absolute temperature T. In the following discussion $\beta(0)$ is referred to, simply but somewhat imprecisely, as the "step energy." The third term is the step–step interaction term, which will not be addressed in this work. Vicinal surfaces whose steps have periodic kinks can be produced by polar and azimuthal rotations about a high symmetry direction, as shown in Fig. 1 of Ref. [5]. At zero temperature the free energy per unit projected area of such a surface is given by

$$f(\phi_0, \theta) = f(0, 0) + (\beta(0) + \epsilon b^{-1} \tan\theta) \tan\phi_0/h. \tag{11}$$

Here θ is the azimuthal angle between a periodically kinked step and a principal axis. ϕ_0 is the tilt angle about this principal axis. b is the spacing between rows of the surface perpendicular to the step edge, so that the one dimensional density of kinks along a straight step edge is $b^{-1}\tan\theta$. ϵ is the energy of an individual kink, called hereafter simply the "kink energy." In terms of the polar angle ϕ between the terrace normal and surface normal, the previous equation is

$$f(\phi, \theta) = f(0, 0) + (\beta(0)\cos\theta + \epsilon b^{-1}\sin\theta)\tan\phi/h. \tag{12}$$

Note that ϕ, ϕ_0 and θ are related by $\tan\phi_0 = \tan\phi\cos\theta$.

3.2. Computational approach

For vanishing azimuthal misorientation, Eq. (12) reduces to

$$f(\phi, 0) = f(0, 0) + \beta(0)\tan\phi/h. \tag{13}$$

All step energies were calculated via Eq. (13). On {001} unreconstructed surfaces of fcc metals, there is just one kind of straight step. The microfacet associated with the step riser is {111}. On {111} unreconstructed surfaces of fcc metals, there are two kinds of straight steps, often called A and B. The A step has a {001} riser, while the B step has a {11$\bar{1}$} microfacet. To find the step energy of a particular straight step, we must compute $f(\phi, 0)$ of a *sequence* of vicinal surfaces which have these steps at various separations. A prescription for choosing the Miller indices of the vicinal surfaces in this sequence is readily available [18,19]. Eq. (13) creates the expectation that a plot of $hf(\phi, 0)$ versus $\tan\phi$ should be a straight line. Accordingly, from a linear fit we obtain the step energy per unit step length β from the slope.

With EAM, particularly as implemented with the Dynamo driver, there is an easier alternative approach for obtaining step energies: with grooved surfaces [5], there is no need for linear fitting. Specifically, it is simple to match the projected areas of the grooved surface and the corresponding flat surface; then the difference of the *total* energies of these two surfaces does

not depend on the terrace energy $f(0,0)$. Calculation of such grooved configurations with ECT, however, would pose formidable difficulties. There are a large number of inequivalent sites, each of which would need to be relaxed independently. No "semiautomatic" way to carry out this process is currently available. Moreover, the need to solve several transcendental equations (i.e. perform several simultaneous relaxations) in ECT would impede the development of a software package which could straightforwardly relax any subset of the individual atoms of the system.

Once we know the step energies, we can proceed to the kink energies, which are calculated via Eq. (12). We consider three kink configurations, one corresponding to each type of step listed above. In each case, we must compute the surface free energies per unit area $f(\phi, \theta \neq 0)$ of a sequence of vicinal surfaces which have the particular kink. (Again, the alternative of grooved notched surfaces [5] is much more difficult with ECT.) Plots of $b[\{f(\phi,\theta) - f(0,0)\}h/\tan\phi - \beta(0)\cos\theta]$ versus $\sin\theta$ are again expected to be a straight lines. From the slopes of a linear fit to these plots, we obtain the energies of the kinks in question.

For all our calculations of $f(\phi,\theta)$ corresponding to Miller indices $\{hkl\}$, only planar relaxations perpendicular to the surface normal, as shown in Fig. 6 of [8], were allowed. As yet there is no clear and unique prescription to determine the number n_{lr} of layers which should be allowed to relax [20]. We chose n_{lr} as the smallest integer greater than the ratio of the lattice constant to the bulk inter-planar spacing of the particular vicinal surface [21], thereby assuring that any atom which does not have the full bulk nn and nnn coordination could relax. Corresponding to these n_{lr} relaxed layers are n_{lr} non-bulk interplanar spacing variables. For each chosen orientation (hkl), we searched for the minimum of ε, determined from Eqs. (1–9), using the simplex [22] algorithm with respect to these n_{lr} spacings. The minimized value of ε (divided by the projected area onto the terrace plane of the vicinal surface) gives the value of $f(\phi,\theta)$ used for the plots. The linearity of the plots was quite good for all the steps and kinks we studied: the standard deviation of the fitted slopes was usually less than 1% of the value of the slope; the fits for ϵ were comparably good to those for β. All values of ECT input parameters were taken from Ref. [15], and our calculation of surface free energies was similar to theirs. However, there is a difference between Refs. [8] and [15] in calculating $R_{ec,1}$: In Ref. [8] an ad hoc screening factor is used for atoms which lie below the top layer of the surface and which lack bulk nn coordination. We followed Ref. [15] in excluding this ad hoc screening.

Before presenting our results, we note that (as implied by the preceding remark) the ECT method is still being refined [20]: the optimal choice of parameters has not been entirely resolved, an explicit treatment of screening appeared and disappeared, and the range of applications has been relatively limited, so that there is not extensive lore about possible problems. In other words, the method cannot, at least yet, be applied in the rather routine, semiautomatic way in which EAM can. Our ECT results should not be taken as definitive but rather as an indication of current capabilities.

4. Results and discussion

The ECT surface free energies per area listed in Table 1 agree with those in Ref. [15] to within a fraction of a percent. (The differences are presumably due to different techniques for solving the non-linear Eqs. (5), (7), (8) and (9) and minimizing the energy ε in Eq. (1).) The results of our calculations for step and kink energies are listed in Table 1. Most of the EAM values are taken from Ref. [5]. (See also Ref. [4].) The most striking difference between the EAM and ECT calculations is that all EAM energies are much lower than their corresponding values from ECT. It has been shown in Ref. [8] that the ECT surface energies are closer to first principles calculations than those from EAM. ECT surface energies also are evidently closer to experimental values [10],

Table 1
Summary of results of our ECT step and kink energy calculations

Surface type	Surface energy in meV/Å²			
	Ag		Pt	
	ECT	EAM	ECT	EAM
(001)	98.6	43.8	147.8	103.1
(111)	76.0	38.5	107.0	90.0

Step type	Step energy β in meV/Å					
	Ag			Pt		
	ECT	(Awning)	EAM	ECT	(Awning)	EAM
(001)/(111)	170	(158)	65	283	(261)	124
(11$\bar{1}$)/(111)	161	(127)	66	274	(171)	123
(111)/(001)	56	(48)	36	90	(52)	
(111)/(110)	−11		−2*	−37		−8*
(100)/(110)	59			100		

Kink type	Kink energy ϵ in meV					
	Ag			Pt		
	ECT	(Awning)	EAM	ECT	(Awning)	EAM
(001)/(111)	213	(219)	102	384	(366)	161
(11$\bar{1}$)/(111)	255	(259)	99	431	(406)	178
(111)/(001)	219	(163)	102	401	(250)	

The values in parentheses are tests of the so-called awning approximation [5], a simple scheme in which β and ϵ are computed directly from [weighted] differences of surface energies, in this case the ECT values listed in the top panel. See text for discussion. The EAM results are from Ref. [5], with two exceptions: the surface energies for Pt were not quoted explicitly there, and the starred values for (110) are estimated from the results tabulated in Ref. [25]. Those two values are the lattice constant times the difference of [relaxed] surface energies per area of the (2 × 1) and (1 × 1) structures (thus neglecting [presumably-significant] step–step interactions).

than those from EAM. However, there is no experimental evidence yet to suggest whether EAM or ECT give a better accounting of step and kink energies.

In our EAM study [5], we found that the step energies could be well approximated by the difference of the surface free energy of the riser microfacet (times the length of the riser) and of the terrace plane (times the length, normal to the step, that is "shaded" by the riser). The feasibility of this so-called awning approximation implies that in EAM the "crease" of the step makes an insignificant contribution to the step energy. In some sense this is a corollary of the finding that EAM energies can be described well by a nearest-neighbor bond approximation [3,5]. In the Table the values in parentheses are from an awning approximation but using our ECT surface free energies. The awning approximation does not work so well here, although for Ag it may still offer a reasonable way to get a quick estimate of energies; the implication is that multisite terms ultimately play a larger role in ECT than in EAM. To further explore this theme, we display in Fig. 1 a Wulff plot of surface free energy (tension) versus orientation along a principal azimuth for which all steps are straight. The plot shows our ECT calculations for Pt and Ag and reproduces the previous trace of EAM values for Ag. The solid curves are arcs of circles which pass through the origin and the surface tensions of the [001] and [111] orientations. In a nearest-neighbor bond approximation, all free energies would lie on these arcs. We see that for Ag the points do lie rather
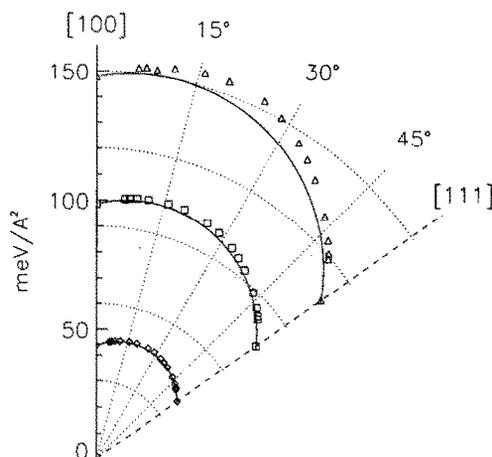
Fig. 1. Segment of the zero-temperature Wulff plot (surface energy versus orientation) along the azimuth connecting the (100) and (111) facets. The values for Pt ($\triangle$) and for Ag ($\square$) were computed using ECT as described in the text. For comparison the values for Ag ($\diamond$) computed earlier with EAM [5] are included. The solid curves for each set are arcs of circles passing through the origin and through the surface energies of the two facets. If only nearest-neighbor interactions determine the surface tensions, all the points would lie on such arcs [24].

close to the arc while for Pt they do not. An implication is that one should be more cautious in accepting results from simple bond-counting schemes for Pt surfaces.

As in EAM [5,25], the energy of the close-packed step on {110} is negative for both Ag and Pt. Thus, both methods suggest, erroneously, that Ag has an instability toward missing-row reconstruction such as occurs for Au{110} (and Pt{110}).

Regarding relative energies, the step on {001} has a much smaller energy than either of those on {111}; the ratio is notably larger than for EAM. The relative size of the two steps on {111} can be assessed in light of Michely and Comsa's [26] elegant STM experiments, from which they deduced that the ratio of the energy of the B step to that of the A step on Pt{111} to be 0.87 ± 0.02 at 700 K. With the ECT values shown in the Table 1 (which are values at 0K) this ratio is $274/283 = 0.968$, closer than the EAM value of 0.991 as found in Ref. [5]. As with EAM, including the leading thermal correction [5] (which lowers the step free energy due to step wandering) decreases the difference between A and B steps, making the ratio closer to unity. A common justification of semiempirical calculations is that they produce the correct trends, even if the overall magnitude is somewhat inaccurate. Note, however, that for Ag{111} ECT and EAM give opposite predictions of the relative energy of A and B steps, and hence their kinks.

There is very little experimental data for kink energies. Poensgen et al. [27] reported a value of 76 meV at 300 K on the Ag(001)/(111) step. This value is somewhat less than values around 100 meV that are found [5,13] using EAM; the ECT value, however, is over twice as large as the EAM numbers. Liu and Adams [13] point out that the experiment is at room temperature and so the theory value, appropriate for $T = 0$, should be reduced by some entropic factor, which to leading order can be estimated from the random wandering of the step [5]. Furthermore, they remark that the measured kink concentrations [27] may not necessarily be the equilibrium concentrations at room temperature but may rather reflect those of some higher temperature, locked in by rapid cooling. Such a quenching effect would further lower the apparent kink energy compared to its zero-temperature value.

5. Summary

We have demonstrated that the ECT method can be applied to calculate the principal step and kink energies of the fcc metals, here Ag and Pt. As with other semiempirical schemes, there are problems in calculating close-packed step energies on the fcc {110} surface. The ECT values are substantially larger than EAM values; for surface energies, these ECT values are in better agreement with theory and experiment, but for steps and kinks there is insufficient evidence to judge. There is better agreement with the experimental value for the ratio of the energies of the two types of steps on Pt{111}. In the case of Ag, ECT and EAM give opposite predictions about the relative energies of these two kinds of close-packed steps and of the associated kinks.

Acknowledgments

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