

Stability of Metal Vicinal Surfaces Revisited

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The stability of metal vicinal surfaces with respect to faceting is investigated using empirical potentials as well as electronic structure calculations. It is proven that for a wide class of empirical potentials all vicinal surfaces between (100) and (111) are unstable at 0 K when the role of third and farther nearest neighbors is negligible. However, electronic structure calculations reveal that the answer concerning the stability of vicinal surfaces is not so clear-cut. Finally, it is shown that surface vibrations at finite temperatures have little effect on the stability of vicinal surfaces.

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The study of energetics of vicinal surfaces is of prime interest for the understanding of various surface processes such as crystal growth, surface morphology, or roughening transition. Recently Frenken and Stoltze [1] raised the important question of the stability of vicinal surfaces in metals. Using a potential based on the effective medium theory (EMT), they predicted that most vicinal surfaces are unstable relative to faceting at 0 K and claimed that the observed stability at room temperature arises from the entropic contribution due to thermal vibrations. In this Letter, we show that the first prediction results entirely from the analytical form and range of interactions of the potential used and that the same conclusion holds for a wide class of empirical potentials. This is in contradiction with calculations based on an explicit determination of the electronic structure which reveals a variety of other behaviors for vicinal surfaces at 0 K. Finally, we show that the vibrational free energy contribution has, most often, a negligible role when calculated correctly.

Let us consider two (low-index) surfaces and denote \mathbf{n}_1, γ_1 and \mathbf{n}_2, γ_2 their normal vector and surface energy (per unit area), respectively, and θ_2 the angle $(\mathbf{n}_1, \mathbf{n}_2)$. Let us also consider a (high-index) surface of surface energy γ and normal \mathbf{n} belonging to the plane defined by $\mathbf{n}_1, \mathbf{n}_2$ and making an angle θ with \mathbf{n}_1 ($0 < \theta < \theta_2$).

An area S of this high-index surface will transform into facets of normal \mathbf{n}_1 (area S_1) and normal \mathbf{n}_2 (area S_2) while keeping its average orientation (Fig. 1) when [2]

$$\gamma S > \gamma_1 S_1 + \gamma_2 S_2, \quad (1)$$

with the constraints $S = S_1 \cos\theta + S_2 \cos(\theta_2 - \theta)$ and $S_1 \sin\theta = S_2 \sin(\theta_2 - \theta)$. It is easy to show that the faceting condition (1) is

$$f(\eta) > (1 - \eta/\eta_2)f(0) + (\eta/\eta_2)f(\eta_2), \quad (2)$$

with $\eta = \tan\theta$ and $f(\eta) = \gamma/\cos\theta$. This simply means that the point $[\eta, f(\eta)]$ must be above the straight line joining the points $[0, f(0)]$ and $[\eta_2, f(\eta_2)]$.

We study here in detail the case of the $p(100) \times (111)$ or $(2p - 1, 1, 1)$ and $p(111) \times (100)$ or $(p + 1, p - 1, p - 1)$ vicinal surfaces and their stability with respect to faceting. These surfaces have close-packed step edges, p atomic rows parallel to the step edge (including the inner edge) in each terrace, and make an angle θ with the (100) surface. The domain $0 < \eta \leq \eta_c$ ($\eta_c = \sqrt{2}/3$) corresponds to (100) vicinal surfaces with p decreasing from infinity to 2 [(311) surface]. The domain $\eta_c \leq \eta < \eta_2$ ($\eta_2 = \sqrt{2}$) is that of (111) vicinal surfaces with p increasing from 2 [(311) surface] to infinity [(111) surface]. Thus the (311) surface can be regarded either as a (111) or a (100) vicinal surface with the highest step density.

As already stated in Ref. [1], $f(\eta)$ falls almost exactly on the straight line joining the points $[0, f(0)]$ and $[\sqrt{2}, f(\sqrt{2})]$. However, there is a small, yet significant, deviation $\Delta f(\eta)$ from this linear behavior and, from Eq. (2), its sign for any intermediate surface determines the stability of this surface with respect to faceting into (100) and (111) facets: If $\Delta f(\eta) > 0 (< 0)$ the vicinal surface is unstable (stable). As noted above, $\Delta f(\eta)$ for the (311) surface plays a special role and is given by

$$\Delta f_{311} = [E_S(311) - E_S(100) - E_S(111)]/S_0^{311}, \quad (3)$$

where $E_S(hkl)$ is the surface energy per surface atom of the (hkl) surface, and S_0^{311} is the area of the projection of the unit cell of the (311) surface on the (100) plane.

In order to distinguish between different energetic contributions, we will first consider a rigid lattice (i.e., without atomic relaxation) at 0 K and calculate the energy with

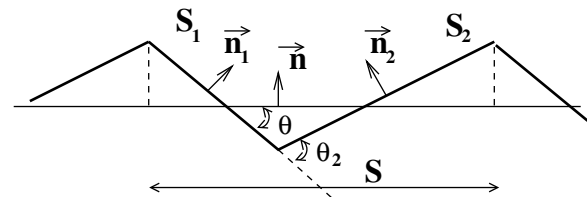


FIG. 1. Faceting.

usual empirical potentials analyzing the effects of the range of interactions and of relaxation. We will also present results from a realistic tight-binding model showing the influence of electronic effects. Finally, the temperature dependence of $\Delta f(\eta)$ will be included with a particular focus on the phonon free energy contribution.

Empirical potentials belonging to a large class can be written as a sum of contributions E_i ($E_i < 0$) of each atom i , i.e.,

$$E = \sum_i E_i = \sum_i \left\{ \sum_{j \neq i} W(R_{ij}) + F \left[\sum_{j \neq i} g(R_{ij}) \right] \right\}. \quad (4)$$

In the following we set $\rho_i = \sum_{j \neq i} g(R_{ij})$. The first term of Eq. (4) is pairwise while the second one (in which g is a positive function) has an N -body character. The functions W and g of the interatomic distance R_{ij} are usually cut off smoothly after a given radius R_c . Pair potentials [$F(\rho_i) = 0$], second moment potentials [$F(\rho_i) \propto \sqrt{\rho_i}$] [3], as well as embedded atom model [4] and EMT potentials [5] belong to this class.

We first fix the interatomic distances to their bulk equilibrium values; i.e., atomic relaxation effects are ignored. With this assumption $\sum_{j \neq i} W(R_{ij})$ and $\sum_{j \neq i} g(R_{ij})$ are linear combinations of the number of neighbors Z_S^i of atom

i in the S th coordination sphere of radius R_S ($R_S < R_c$) and $E_i = E(Z_1^i, \dots, Z_S^i, \dots)$. It is usual to take R_1 as the reference distance and set $g(R_1) = 1$.

When the range of the potential is restricted to the first and second neighbors only, it can be shown [6] that the step energies (per step atom) $E_{step}^{(100) \times (111)}(p)$ and $E_{step}^{(111) \times (100)}(p)$ do not depend on p ; i.e., there is no interaction between steps even when $p = 2$. Then it can be proven that the curve $\Delta f(\eta)$ is made of two straight lines, the slopes of which are a function of the corresponding step energy and of $\gamma(100)$ and $\gamma(111)$. These two lines meet at the intermediate point $(\sqrt{2}/3, \Delta f_{311})$ and the sign of Δf_{311} determines the stability of the vicinal surfaces. A counting of coordination numbers leads to

$$\Delta f_{hkl} = [E(7, 3) + E(10, 5) - E(8, 5) - E(9, 3)]/S_0^{hkl}, \quad (5)$$

in which the first two terms refer to the outer and the inner step edges, respectively, and the last two terms to a (100) and (111) surface atom. S_0^{hkl} is the projected area of the (hkl) surface unit cell on the (100) surface. In the case of a pair potential Δf_{hkl} is strictly equal to 0 so that the energy of any vicinal surface is equal to the energy of the faceted (100)–(111) surface. Thus, when the potential includes an N -body contribution, Δf_{hkl} can be written

$$\Delta f_{hkl} = \{[F(7 + 3g_2) - F(9 + 3g_2)] - [F(8 + 5g_2) - F(10 + 5g_2)]\}/S_0^{hkl}, \quad (6)$$

with $g_2 = g(R_2)$. For all the existing potentials of the form (4) $F''(\rho) = d^2F/d\rho^2$ is positive. As a consequence, $F(\rho - 2) - F(\rho)$ is a decreasing function of ρ and therefore Δf_{hkl} is always positive and in particular Δf_{311} . This common property of this class of potentials has a clear physical origin: The energy E_i of an atom i should decrease more and more slowly when its coordination increases towards the bulk coordination [7]. It clearly implies that $F''(\rho)$ must be positive. We have then proven that for *any* empirical potential of the general form (4) on a rigid lattice at 0 K and a cutoff radius $R_c < R_3$, *any* vicinal surface from (100) to (111) is *unstable* with respect to faceting. As an example, we show in Fig. 2 the result of a calculation for Cu with a potential denoted P_2 in which $W(R_{ij}) = A(R_1/R_{ij})^p$, $F(\rho_i) = -\xi\rho_i^{2/3}$, and $g(R_{ij}) = \exp[-2q(R_{ij}/R_1 - 1)]$.

When the range of the potential is extended to further neighbors ($R_c \geq R_3$) this result is no longer valid. First, for a general potential, steps with narrow terraces start to interact and the curve $\Delta f(\eta)$ is no longer made of two straight lines. The pair potential does not contribute to this interaction at least when $R_c < R_5$ but it gives a contribution $-4W(R_3)/S_0^{311}$ to Δf_{311} which tends to destabilize (stabilize) the vicinal surfaces when $W(R_3)$ is negative (positive). Moreover, additional terms due to other sites appear in Eqs. (5) and (6), and therefore the sign of the contribution of the N -body function F to Δf_{311} cannot be

inferred since it depends on the magnitude of g_3, g_4, \dots . This is shown in Fig. 2 in which $\Delta f(\eta)$, obtained with a potential P_4 of the same functional form as P_2 but with $R_4 < R_c < R_5$, is drawn. In this potential the role played by third and fourth neighbors is sufficient to reverse the

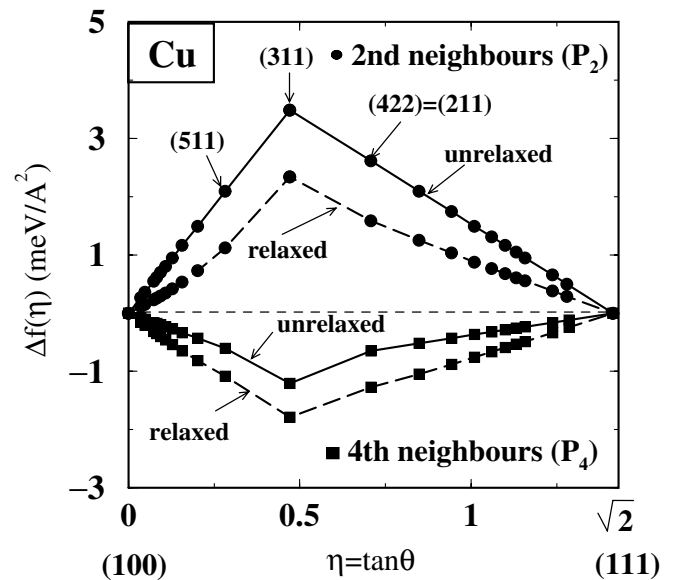


FIG. 2. $\Delta f(\eta)$ for Cu from empirical potential calculations up to second and fourth neighbors, with and without relaxations.

sign of Δf_{311} . Thus, the range of the potential may play a crucial role on the stability of vicinal surfaces.

Furthermore, the potentials discussed above have a common drawback: The energy of an atom i is completely fixed by its coordination numbers Z_S^i whereas it should also depend on the angular disposition of its neighbors. This effect is accounted for in electronic structure calculations which, moreover, include long range interactions (often oscillatory). These interactions, although small, may play a role in the very delicate energy balance which determines the stability of vicinal surfaces. In a recent paper [8], we calculated the step energies of various vicinal surfaces from a realistic tight-binding model for Rh, Pd, and Cu. The functions $\Delta f(\eta)$ derived from the results of this paper are plotted in Fig. 3 for the (100) and (111) vicinal surfaces.

As can be seen there is a great variety of shapes. For Cu the curve is below the straight line and the vicinal surfaces are stable at 0 K while for Pd they are unstable. For Rh all vicinal surfaces are stable with respect to faceting into (100) and (111) surfaces. However, the curve presents two local minima at $\eta = \sqrt{2}/5$ [(511) surface] and $\eta = 3\sqrt{2}/5$ [(533) surface] with a local maximum at $\eta =$

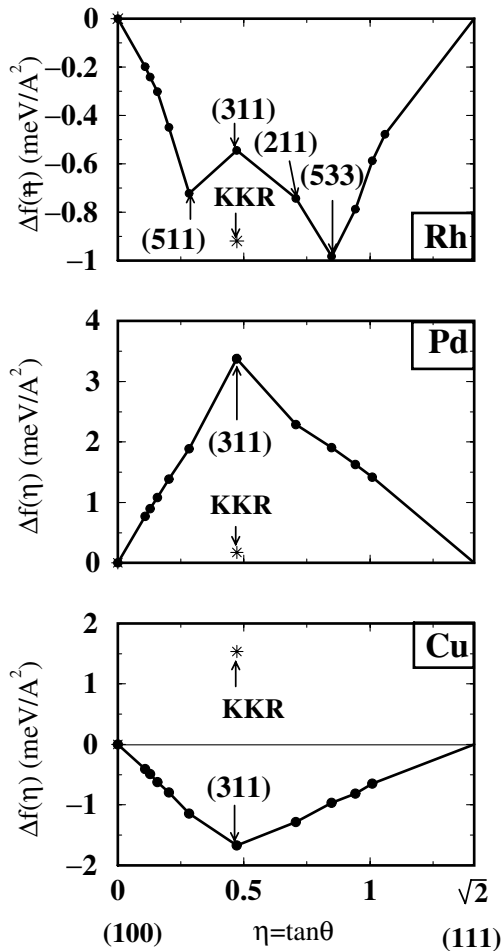


FIG. 3. $\Delta f(\eta)$ for Rh, Pd, and Cu from tight-binding [8] and Korringa, Kohn, and Rostoker (KKR) [9] calculations.

$\sqrt{2}/3$ [(311) surface]. This means that the vicinal surfaces of orientation such that $\sqrt{2}/5 < \eta < 3\sqrt{2}/5$ are unstable relative to faceting into (511) and (533) orientations. This peculiar behavior is related to electronic step-step interactions which are repulsive for the (311) and (211) surfaces and attractive for (511) and (533) surfaces [8]. We have also plotted points deduced from Eq. (3) using the *ab initio* calculations of Galanakis *et al.* [9] on the three surfaces (111), (100), and (311) of Cu, Pd, and Rh. For Rh and Pd the *ab initio* calculations are in qualitative agreement with our results but for Cu they predict at least an unstable range of orientations.

Until now we have neglected the effect of atomic relaxations. Relaxation leads to a decrease of the surface energies by a few percents (up to 10%) and one could wonder if, in view of the small value of $\Delta f(\eta)$, it could change the results obtained on the rigid lattice. However, it must be kept in mind that the stability depends on energy differences [Eq. (3)]. Thus, some kind of cancellation is expected. Actually, we have performed a full energy minimization using the potentials P_2 and P_4 and, in both cases (Fig. 2) it acts in favor of the stabilization since the relaxation is larger on a vicinal surface than on a flat one. Nevertheless, this effect is not large enough to modify the stability (or instability) of a surface, and the results obtained on the rigid lattice remain qualitatively valid except when $\Delta f(\eta)$ is positive but very small. Besides the lowering of $\Delta f(\eta)$, relaxation effects modify its shape. In particular, when using the potential P_2 , the curves joining, on the one hand, the (100) and (311) points and, on the other hand, the (311) and (111) points are no longer straight lines but get a positive curvature due to the repulsive elastic step-step interactions.

The above study sheds light on the results of Frenken and Stoltze [1] at 0 K. These authors have calculated $\Delta f(\eta)$ for the fully relaxed (100) and (111) vicinal surfaces of Ag using an EMT potential with $R_3 < R_c < R_4$ [10] but in which the role played by third neighbors is very small compared to that of first and second neighbors as well in the pair as in the N -body part of the potential (to fix ideas, $g_1 = 1, g_2 \approx 3 \times 10^{-2}, g_3 \approx 3 \times 10^{-3}$). Our analysis shows that all the $\Delta f(\eta)$ curves calculated with a potential of type (4) and a cutoff radius $R_c < R_3$ will behave identically: This explains the strong similarity between our results on relaxed Cu with potential P_2 and those of Frenken and Stoltze for Ag. Therefore the instability of vicinal surfaces at 0 K is an unavoidable consequence of the type of potentials and range of interactions used in Ref. [1]. However, these potentials may be not accurate enough. Indeed, electronic structure calculations predict other possible behaviors at 0 K. Vicinal surfaces can be stable or unstable relative to faceting into (100) and (111) facets or they can also present a faceting into other high index surfaces.

Let us now consider the influence of a finite temperature. $\Delta f(\eta)$ varies with temperature due to the excess

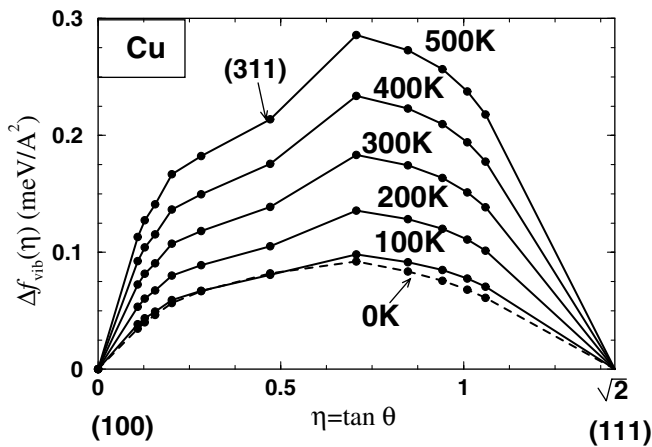


FIG. 4. $\Delta f_{\text{vib}}(\eta)$ for Cu from potential P_2 .

vibrational free energy and to the entropy gained by the meandering of steps. As stated in Ref. [1], the meandering entropy has a stabilizing effect but it is negligible at room temperature for Cu and Ag. This is *a fortiori* true for Rh and Pd in which the formation energy of a kink is much larger than in noble metals. The excess vibrational free energy has two contributions: the internal energy which dominates at low temperature and vanishes at high temperature, and the entropy part which has the inverse behavior. Indeed Eq. (5) applies to any energy, and, in particular, to the vibrational free energy provided that the contribution of an atom i is completely determined by its numbers of neighbors inside the first two coordination spheres, at most. It is seen that besides the vibrational entropic energy estimated by Frenken and Stoltze in an isotropic Einstein model as coming from the difference between the outer edge and a (111) surface atom, i.e., $E(7, 3) - E(9, 3)$, another term *should* be considered, namely, $E(10, 5) - E(8, 5)$ arising from the difference between the inner edge and a (100) surface atom. These two terms have opposite signs and are expected to be of the same order of magnitude. Thus, the calculation of the contribution of vibrational free energy $\Delta f_{\text{vib}}(\eta)$ to $\Delta f(\eta)$ needs a precise knowledge of the vibration spectra of the bulk metal as well as of the flat and vicinal surfaces and should include the internal energy part (omitted in Ref. [1]), at least at low temperatures. We have recently shown that a potential of type P_2 is able to reproduce very accurately the experimental data for the vibration spectra of the bulk Cu and of its low- and high-index surfaces [11]. We have used these vibration spectra to calculate $\Delta f_{\text{vib}}(\eta)$ as a function of temperature (Fig. 4).

Two main conclusions can be drawn from the results: First, the order of magnitude is approximately some tenths

of $\text{meV}/\text{\AA}^2$; secondly, $\Delta f_{\text{vib}}(\eta)$ is positive. Consequently, not only phonons have a very small effect on the stability of vicinal surfaces but their contribution to the energy balance tends to destabilize the vicinal surface, at least for Cu, contrary to what is claimed in Ref. [1]. This does not mean that the vibrational free energy is always negligible. For instance, it will play a role in the temperature dependence of the step-free energy [12] and, thus, on the thermal roughening.

In summary, we have shown that the energy balance which drives the stability of vicinal surfaces at 0 K is very delicate and that the result may depend on the method used to calculate the total energy. This means that many behaviors can occur, namely, stability or instability relative to faceting into low-index as well as high-index orientations. Furthermore, the contribution of thermal vibrations is small, and it is unlikely that it stabilizes vicinal surfaces that are unstable at 0 K.

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