Novel Method for the Experimental Determination of Step Energies

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We describe a novel method for the determination of the absolute step energies using the temperature dependence of the equilibrium shape of adatom or vacancy islands. The method is demonstrated with islands on the Cu(111) surface.

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The free energy of steps of monatomic height is one of the most important energetic parameters in the physics of crystalline solids. It controls the size of facets in the equilibrium shape of crystals and the curvature of rough surfaces [1]. It is likewise an important parameter in the stability of vicinal surfaces against step bunching transitions [2,3] and transitions involving a reconstruction of the surface [4,5]. Furthermore, the minimization of the step energy is the driving force for coarsening processes on surfaces, e.g., for the growth of larger islands at the expense of smaller ones, the decay of mounds during and after epitaxial growth [6–13], and for the decay of nanostructures in general. Last but not least, the equilibrium shape and the shape fluctuations of monatomic high islands (2D islands) on surfaces, and thereby also the migration of entire islands on surfaces, depend on the step-free energy [14–16]. The ubiquity of the step-free energy as the controlling parameter in many phenomena should provide ample means to determine its magnitude. This is, however, not so. The traditional way to determine the step energy from the equilibrium shape of crystals is barred with many nontrivial experimental difficulties and additionally requires as an input the free energy of the flat surfaces [17,18], which in turn is not known very accurately. The step-free energy derived from the chemical potential of islands as observed in Ostwald ripening of islands appears to be unrealistically high for reasons hitherto not understood [12]. An average step energy was recently calculated from the size dependence of the Brownian motion of islands using a continuum model [15] for the step fluctuations [19]. Possible systematic errors of the method are not known presently. Relying entirely on first principles theoretical calculation is likewise not a remedy to the situation as it seems that different respectable approaches [20,21] yield rather different results [0.38 and 0.26 eV/atom for B steps on Cu(111), respectively]. While the determination of the absolute value of the step-free energy is a problem, the variation of the step energy as a function of the orientation can be measured straightforwardly from the equilibrium shape of 2D islands. Michely *et al.*, e.g., have determined the ratio of the energies of A and B steps on Pt(111) from island equilibrium shapes [22]. Since 2D islands have no facets at finite temperature the complete orientational dependence of the step-free energy is obtained from the equilibrium shape using an "inverse" Wulff plot [1].

In this Letter we describe a novel method to determine the absolute value of step energies from experimental data on the equilibrium shape of 2D islands as a function of temperature. The method is based on the fact that the leading term in the temperature dependence of the free energy of a step oriented at midangle between the two densely packed directions (i.e., a 100% kinked step) is controlled by a zero point entropy term for which an analytical expression is easily derived.

The contour lines for such a step are plotted in Figs. 1(a) and 1(b) as solid lines for the square and the hexagonal lattice, respectively. The step contour changes direction after each length unit, equivalent to an atom diameter a. For the moment we assume that the energies associated with the various paths depicted as dashed lines in Figs. 1(a) and 1(b) are sufficiently close to each other so that the leading term in the configurational partition function for the step is the entropy associated with microscopic realizations of the steps shown as dotted lines in Figs. 1(a)

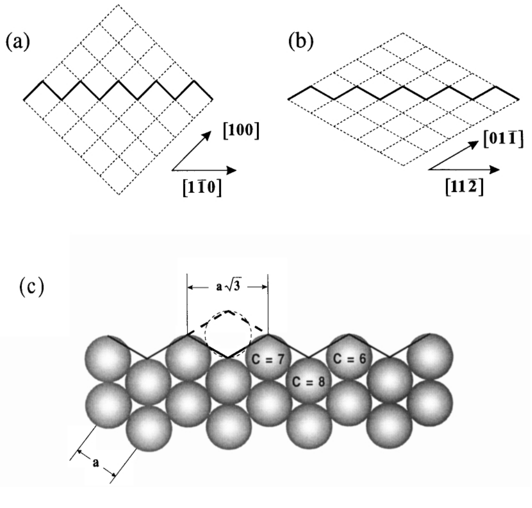

FIG. 1. $N = 10$ length units of the 100% kinked steps (solid lines) for a (a) square lattice and (b) hexagonal lattice. The orientation is along the $\langle 011\rangle$ direction and the $\langle 11\bar{2}\rangle$ direction, respectively. The ensemble of dashed lines represent paths which have the same microscopic length and therefore nearly the same energy (see text for discussion). (c) Structure of a $\langle 11\bar{2}\rangle$ oriented step (solid line) on a (111) surface. In the macroscopic limit only configurations which correspond to adding the dashed atom or removing a kink atom from the step contribute to the free energy. Coordination numbers C are indicated for three edge atoms ($C = 7$ is with the added atom).

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and 1(b). The number of paths for a step consisting of N length units equals the number of possibilities Z in a coin tossing game to have in N tosses exactly $N/2$ results "$+1$" and $N/2$ results "-1." The number of possibilities is $Z = N!/[(N/2)!]^2$ ([23], Sec. 67ff.). For large N, the entropy is therefore

$$S_{N\to\infty} = k_B \ln Z = N k_B \ln 2 \,. \tag{1}$$

As seen from the factor ln2 (and the derivation of the equation) only two paths per atom contribute to the entropy. These paths correspond to adding the dashed atom or removing the atom with $C = 6$ from the step [Fig. 1(c)]. In general, these crucial paths may have a different energy. By expanding the partition function per atom $Z_a = \exp[-(E - \Delta E_b/2)/k_B T] + \exp[-(E + \Delta E_b/2)/k_b T]$, with E the mean energy of the two paths and ΔE_b the difference, to first order in ΔE_b one obtains instead of Eq. (1)

$$S_{N\to\infty} \cong N k_B \ln\left[2 + \left(\frac{\Delta E_b}{2 k_B T}\right)^2 \dots\right]. \tag{2}$$

As shown later, the additional term involving the energy difference is small for Cu(111) and can be neglected.

We are interested in the entropy per step length S which is $S = S_N \sqrt{2}/a$ and $S = 2 S_N / a\sqrt{3}$ for steps on a square and a hexagonal lattice, respectively. The free energy β for a step oriented along the $\langle 11\bar{2}\rangle$ directions on a hexagonal surface is therefore

$$a\beta_{\langle 11\bar{2}\rangle}(T) = a\beta_{\langle 11\bar{2}\rangle}(T = 0) - k_B T \,\frac{2\ln 2}{\sqrt{3}} \,. \tag{3}$$

For steps with the mean orientation along the direction of dense packing the free energy can be expressed in terms of the energy ε_k necessary to create a kink of one atom length in that step. To first order in $\exp(-\varepsilon_k/k_b T)$ the partition function per step atom is $Z = e^{-a\beta_{\langle 01\bar{1}\rangle}(T=0)/k_B T}(1 + 2e^{-\varepsilon_k/k_B T})$ and the free energy is therefore

$$a\beta_{\langle 01\bar{1}\rangle}(T) = a\beta_{\langle 01\bar{1}\rangle}(T = 0) - 2 k_B T e^{-\varepsilon_k/k_B T}. \tag{4}$$

The ratio of the free energies of the 100% kinked and nearly straight steps is

$$\frac{\beta_{\langle 11\bar{2}\rangle}(T)}{\beta_{\langle 01\bar{1}\rangle}(T)}\left(1 - \frac{2 k_B T e^{-\varepsilon_k/k_B T}}{a\beta_{\langle 01\bar{1}\rangle}(0)}\right) = \frac{\beta_{\langle 11\bar{2}\rangle}(0)}{\beta_{\langle 01\bar{1}\rangle}(0)} - \frac{2 k_B \ln 2}{\sqrt{3}\, a\beta_{\langle 01\bar{1}\rangle}(0)}\, T \,. \tag{5}$$

An analogous equation can be derived for the square lattice. Because of the symmetry of the hexagonal lattice, the ratio of the free energy $\beta_{\langle 11\bar{2}\rangle}/\beta_{\langle 01\bar{1}\rangle}$ is equal to the ratio of the distances from the island center to the perimeter with the corresponding orientations. We note that Eq. (5) and the equivalent one for the square lattice can also be derived from the analytical forms of the equilibrium shapes in the Ising model [24,25], but the validity does not depend on the special assumptions of the Ising model. Equation (5) is accurate to first order in $\exp(-\varepsilon_k/k_B T)$. Comparison to the exact form of the equilibrium shape in the Ising model shows that the approximation is excellent for temperatures $T < 0.6\varepsilon_k/k_B$ (here $T \leq 750$ K).

Using Eq. (5) the absolute value of the step energy $a\beta_{\langle 01\bar{1}\rangle}(T = 0)$ can be determined from a plot of experimental data of the ratios of the free energies vs T by recursion: A first estimate on the step energy is obtained from the slope of the ratios of the free energies vs T, neglecting the kink term on the left side of Eq. (5). In a second round, the estimate for the step energy and the kink energy ε_k are used to calculate the term involving the kink energy. Then, the left hand side of Eq. (5) is plotted vs the temperature T once more to obtain a refined value for step energy, and so forth. The procedure converges rapidly so that only about three iterations are required. The kink energy can be determined independently, e.g., from the spatial correlation function of steps on vicinal surfaces [26], from fitting the island shape to the analytical shape function of the Ising model [25], or from an Arrhenius plot of the curvature of the island in the section where the curvature is the least [27].

The correction term in Eq. (2) containing the energy difference ΔE_b of the two crucial paths depicted in Fig. 1(c) can be neglected if $(\Delta E_b/2 k_B T)^2$ is small compared to ln2. In order to estimate whether this is a severe limitation to the applicability of Eq. (5) we estimate ΔE_b from the nearest-neighbor effective medium theory model [28]. In this model, the energy $E_b(C)$ of an atom in an arbitrary site becomes a nonlinear function of its nearest-neighbor coordination C. Considering the number of nearest neighbors the energy difference between the two step configurations in Fig. 1(c) is

$$\Delta E_b = E_b(6) + E_b(8) - 2E_b(7) \,. \tag{6}$$

ΔE_b would be zero if the energy were a linear function of the coordination number between $C = 6$ and $C = 8$. Using a parametrized form of $E_b(C)$ for the Cu(111) surface, e.g., from [28] ($E_b = -1.924 - 0.159C + 0.0023C^2$ eV), a difference $\Delta E_b = 4.6$ meV is calculated. This changes the slope at 300 K by only 0.6%. We therefore conclude that for Cu(111) Eq. (5) holds in a wide temperature range from below 300 K up to about 750 K.

Our method neglects vibrational contributions to the step-free energy which requires consideration. For steps on Cu(100) surfaces, the vibrational free energy is linear in the temperature above 300 K [29]. With a term linear in the temperature taken into account, Eq. (5) is to be modified such that the term ln2 is replaced by

$$\ln 2 \to \ln 2 + \hat{\beta}^{(\mathrm{vib})}_{\langle 11\bar{2}\rangle} - \hat{\beta}^{(\mathrm{vib})}_{\langle 01\bar{1}\rangle} \,. \tag{7}$$

Here $\hat{\beta}^{(\mathrm{vib})}_{\langle 11\bar{2}\rangle} - \hat{\beta}^{(\mathrm{vib})}_{\langle 01\bar{1}\rangle}$ denotes the difference in the vibrational free energies per atom in units of $k_B T$ for the kinked step and the straight step, respectively. A rough estimate of the difference is obtained by scaling the frequencies with the square root of the coordination number of the atoms, a procedure which leads to qualitative agreement with calculated vibrational step-free energies [29]. The result for the difference $\hat{\beta}^{(\mathrm{vib})}_{\langle 11\bar{2}\rangle} - \hat{\beta}^{(\mathrm{vib})}_{\langle 01\bar{1}\rangle}$ is -0.008 which amounts to 1% of ln2. Vibrational contributions can therefore be neglected.

On the (111) surface of an fcc crystal two crystallographically different densely packed steps exist. These A and B steps display the (100) facet and the (111) facet, respectively. The energies of the two types of steps need not be the same. Accordingly the symmetry of the equilibrium shape reduced from hexagonal to trigonal. Equation (5) is easily generalized to the trigonal case with different energies for the A and B steps by replacing $\beta_{\langle 01\bar{1}\rangle}$ by β_A and β_B, and the kink energy ε_k by ε_A and ε_B, respectively. For a trigonal shape, the ratios of the free energies in Eq. (5) are no longer equal to the ratios of the radii to the corners and the straight sections but must be determined from the equilibrium shape by an inverse Wulff construction.

We now apply the method to experimental data obtained on the Cu(111) surface. Equilibrium shapes of islands were studied using a variable temperature scanning tunneling microscope of the Besocke type. For details of the sample preparation the reader is referred to [12]. In the temperature range of our investigation $(300 < T < 380\ \mathrm{K})$ the diffusion along the perimeter of the islands is fast enough so that the islands have their equilibrium shape, save for spatiotemporal fluctuations which are quite large for the islands' sizes studied here (4000–9000 atoms). In order to average over these fluctuations we have averaged 110–180 island shapes for each temperature. In total 2000 adatoms and vacancy islands were evaluated. Special care was taken to restrict the analysis to islands which showed no noticeable contamination over a period of several hours. The averaged island shapes were also corrected for a possible distortion of the images due to the hysteresis of the piezo actuators of the STM. Three out of a total of 15 averaged equilibrium shapes are shown in Fig. 2. The shapes are nearly hexagonal which means that the energies for A and B steps and also the kink energies are nearly equal. We find the ratio of the two energies to be $\beta_A/\beta_B = 0.989 \pm 0.005$, consistent with an earlier but less accurate result [30]. While the ratio differs slightly from unity we can safely neglect the small deviation in the following considerations. Using the 15 equilibrium shapes we have determined the kink energy by fitting the analytical form of the shape for an Ising island to the experimental data. The kink energy is the only parameter in the model. The resulting kink energy is $\varepsilon_k = 0.110 \pm 0.005$ eV. The same number within the statistical error is obtained if one fits only the curvature in the nearly straight sections of the island edge to an analytical expression which relates curvature, line tension, and diffusivity of the step, or from an Arrhenius plot of the curvature [27]. The kink energy is in the expected range, 15% smaller than the kink energy for steps on the Cu(100) surface [26].

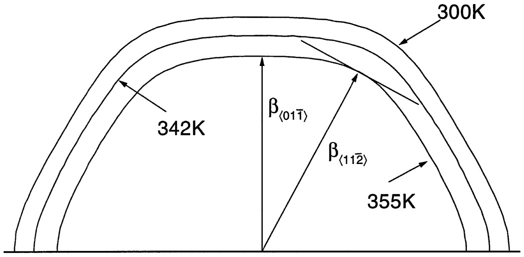

FIG. 2. Upper half of the equilibrium shapes of adatom islands on Cu(111) at three different temperatures. The lines represent unsmoothed connecting lines between individual data points (not shown). The distances to the tangents of the island perimeters are proportional to the free energies β.

The ratio of the free energies of the steps, $\beta_{\langle 11\bar{2}\rangle}/\beta_A$ and $\beta_{\langle 11\bar{2}\rangle}/\beta_B$, were determined from an inverse Wulff plot. From the slope of the mean value $(\beta_{\langle 11\bar{2}\rangle}/\beta_A + \beta_{\langle 11\bar{2}\rangle}/\beta_B)/2$ plotted vs temperature a first value for $\beta_{A/B}(T = 0)$ is obtained which was then used to calculate the correction term containing the kink energy. Figure 3 displays the converged result. From the slope and the intersection with the y axis one obtains

$$\begin{aligned} \beta_{A/B}(T = 0) &= 0.31 \pm 0.04\ \mathrm{eV}/a\,, \\ \beta_{\langle 11\bar{2}\rangle}(T = 0)/\beta_{A/B}(T = 0) &= 1.13 \pm 0.01\,. \end{aligned} \tag{8}$$

The quoted error includes the error in the determination of the kink energy.

The ratio $\beta_{\langle 11\bar{2}\rangle}/\beta_{A/B}$ for $T = 0$ is slightly smaller than $2/\sqrt{3} = 1.155$, which would be the ratio in the Ising

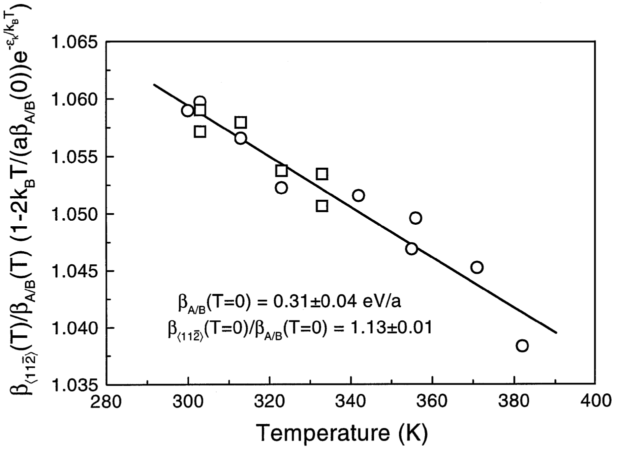

FIG. 3. The experimentally determined ratios of the step-free energies for steps oriented along the $\langle 11\bar{2}\rangle$ and $\langle 011\rangle$ directions multipled by the kink term on the left hand side of Eq. (5) plotted vs the temperature. Circles and squares refer to adatom and vacancy islands, respectively. The absolute step energy is proportional to the inverse of the slope.

model and in a nearest-neighbor model with the binding energy $E_b(C)$ being a linear function of the coordination number. However, the difference is hardly outside the statistical error. The result for the step energy obtained here is significantly lower than the 0.5 eV per atomic distance a obtained in island decay studies [12]. The difference is far outside the experimental error. While the reason for this discrepancy is not clear, it is obvious from a comparison to step energies of other materials [31] that the value derived from the effective chemical potential controlling the island decay must be too high. The present result is higher than the result obtained from an analysis of the Brownian motion of adatom and vacancy islands on the same surface ($\beta_{A/B} = 0.22 \pm 0.02$ eV$/a$) [19]. Using the semiempirical embedded atom model Karimi *et al.* [32] find a step energy of 0.26 eV$/a$. A tight-binding model with many-body corrections produces 0.24 eV$/a$ [33]. Recently, two first principles calculations for the step energies on Cu(111) became known which produced surprisingly different numbers (0.38 and 0.26 eV$/a$ for the B step [20,21]. Given the large scattering in the data, both on the theory side as well as for the two entirely different experimental approaches, it appears difficult to argue what the true value might be.

In summary we have demonstrated a new method to determine the absolute value of step energies from equilibrium island shapes. The method is applicable to quadratic as well as to trigonal lattices. For trigonal lattices, the different energies of A and B steps can be determined independently. The requirement that the energy difference between the two lowest energy states of the 100% kinked step must be smaller than $2k_BT$ can presumably be met in most cases by analyzing data at not too low T. Otherwise, the step energy could still be obtained from a self-consistent fit of generalized forms of Eq. (5) to the experimental results, provided that a sufficiently large and accurate database is available. In most cases, the lower limit in the temperature will be set by the requirement that the diffusion along the island perimeter must be rapid enough to ensure that the islands have assumed their equilibrium shape.

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[1] M. Wortis, in *Chemistry and Physics of Solid Surfaces*, edited by R. Vanselow and R. Howe (Springer, New York, 1988), Vol. 7, p. 367.
[2] E. D. Williams and N. C. Bartelt, Ultramicroscopy **31**, 36 (1989).
[3] E. D. Williams, Surf. Sci. **299/300**, 502 (1994).
[4] A. Bartolini, F. Ercolessi, and E. Tosatti, Phys. Rev. Lett. **63**, 872 (1989).
[5] E. D. Williams, R. J. Phaneuf, J. Wei, N. C. Bartelt, and T. L. Einstein, Surf. Sci. **294**, 219 (1993).
[6] M. Breeman, G. T. Barkema, and D. O. Boerma, Surf. Sci. **303**, 25 (1994).
[7] H. P. Bonzel and W. W. Mullins, Surf. Sci. **350**, 285 (1996).
[8] N. C. Bartelt, W. Theis, and R. M. Tromp, Phys. Rev. B **54**, 11 741 (1996).
[9] K. Morgenstern, G. Rosenfeld, and G. Comsa, Phys. Rev. Lett. **76**, 2113 (1996).
[10] K. Morgenstern, G. Rosenfeld, E. Laegsgaard, F. Besenbacher, and G. Comsa, Phys. Rev. Lett. **80**, 556 (1998).
[11] U. Kürpick, P. Kürpick, and T. S. Rahman, Surf. Sci. **383**, L713 (1997).
[12] G. S. Icking-Konert, M. Giesen, and H. Ibach, Surf. Sci. **398**, 37 (1998).
[13] C. Klünker, J. B. Hannon, M. Giesen, H. Ibach, G. Boisvert, and L. J. Lewis, Phys. Rev. B **58**, R7556 (1998).
[14] K. Morgenstern, G. Rosenfeld, B. Poelsema, and G. Comsa, Phys. Rev. Lett. **74**, 2058 (1995).
[15] S. V. Khare and T. L. Einstein, Phys. Rev. B **54**, 11 752 (1996).
[16] S. V. Khare and T. L. Einstein, Phys. Rev. B **57**, 4782 (1998).
[17] J. M. Bermond, J. J. Métois, X. Egéa, and F. Floret, Surf. Sci. **330**, 48 (1995).
[18] K. Arenhold, S. Surnev, H. P. Bonzel, and P. Wynblatt, Surf. Sci. **424**, 271 (1999).
[19] D. C. Schlößer, L. K. Verheij, G. Rosenfeld, and G. Comsa, Phys. Rev. Lett. **82**, 3843 (1999).
[20] L. Vitos, H. L. Skriver, and J. Kollár, Surf. Sci. **425**, 212 (1999).
[21] P. Feibelman, Phys. Rev. B **60**, 11 118 (1999).
[22] T. Michely and G. Comsa, Surf. Sci. **256**, 217 (1991).
[23] W. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, New York, 1968), Vol. I.
[24] R. K. P. Zia and J. E. Avron, Phys. Rev. B **25**, 2042 (1982).
[25] R. K. P. Zia, J. Stat. Phys. **45**, 801 (1986).
[26] M. Giesen-Seibert, F. Schmitz, R. Jentjens, and H. Ibach, Surf. Sci. **329**, 47 (1995).
[27] G. S. Icking-Konert, M. Giesen, and H. Ibach (to be published).
[28] P. Stoltze, J. Phys. Condens. Matter **6**, 9495 (1994).
[29] A. Kara, S. Durukanoglu, and T. S. Rahman, Phys. Rev. B **53**, 15 489 (1996).
[30] M. Giesen, U. Linke, and H. Ibach, Surf Sci **389**, 264 (1997).
[31] H. P. Bonzel, Surf. Sci. **328**, L571 (1995).
[32] M. Karimi, T. Tomkowski, G. Vidali, and O. Biham, Phys. Rev. B **52**, 5364 (1995).
[33] P. Hecquet and B. Salanon, Surf. Sci. **366**, 415 (1996).