# Step doubling and related transitions on vicinal surfaces

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We discuss two types of step-height doubling transitions on vicinal surfaces. In one type, exemplified by Ge(111)-[$1\bar{2}1$], a phase transition can occur since the symmetry between alternate terraces is broken at low temperatures. There is evidence in both experiment and in Monte Carlo simulations that this transition can have Ising character. In the second type, exemplified by Si(001)-[110], one subset of terraces is always favored, so that no symmetry is broken. If an actual phase transition occurs (rather than a smooth crossover), it is expected to be first order, implying a coexistence region in a temperature-misorientation phase diagram. Finally, the coalescence of steps into steps of height more than two atomic layers is briefly considered.

## I. INTRODUCTION

An intriguing aspect of vicinal surfaces is the coalescence of single-layer height steps into double-height steps as the temperature or misorientation angle is varied. Questions of concern are whether this coalescence represents an actual phase transition; is the transition first or second order; if second order, what is the universality class; and what can be learned about interactions between steps. In this short paper, we shall discuss two distinct prototypes for step-height doubling.

We approach the problem by labeling the terraces separated by single-layer height steps as *A* and *B*, alternately. Thus, if all the single-layer height steps coalesced into doubles, we would have only *A* terraces or only *B* terraces. If the *A* and *B* terraces are identical (except for a simple translation)—or, equivalently, the step from *A* down to *B* is identical to the step from *B* down to *A*—then above the transition *A* and *B* terraces should by symmetry occur in equal abundance; below the transition, one or the other predominates. This picture is an example of "spontaneous symmetry breaking." We have studied what we believe to be a physical example of this symmetry breaking, Ge(111)-[$1\bar{2}1$], using low-energy electron diffraction (LEED); additionally, we have performed Monte Carlo simulations of related simple models.

In an alternate scenario, there is some intrinsic difference between *A* and *B* terraces, so that either *A* or *B* terraces are always favored, though to a much greater degree once the double-height steps appear. In this case, no symmetry is broken. An example is the much-discussed case of Si(001)-[110]. Lacking any symmetry breaking, only local changes in properties of the surface *need* occur as temperature or misorientation angle is changed. In this case one expects changes in behavior as temperature or misorientation angle is varied to be either smooth (with no transition at all) or to occur through *first*-order transitions.[1]

## II. ISING-LIKE STEP-DOUBLING TRANSITIONS

First, we consider a system in which energy favors the coalescence of two single-layer height steps into a double-layer height step. Barring a perversely greater kink energy for singles than doubles, entropy will favor the breakup of the step into two singles at sufficiently high temperature. In the limit of an isolated double-layer height step, i.e., in the limit of vanishing misorientation angle, a phase transition occurs when the temperature rises to the point at which twice the free energy per unit length of a single-height step drops to equal the free energy per unit length of a double-height step. This transition, depicted schematically in Fig. 1, is an example of the wetting transition explored a decade ago in the context of steps by Chui and Weeks.[2] Above the transition, the new intermediate terrace "wets" in the sense that the two single-height steps are unbound.

The next question is what happens when there is a dense collection of double-layer height steps. Figure 2 illustrates, for the case when both the energy per unit length and the kink energy of a single-layer height step are equal to those of a double-layer height step, that double-layer height steps predominate at low temperature while singles predominate at high temperature. As described in the introduction, we label the terraces as *A* and *B*, alternately. Above the transition, there should be equal areas of each, while below the transition, the area of *A* or of *B* (with equal probability) should predominate, breaking the symmetry. To determine the universality class associated with this transition, one should first determine the order parameter; the answer is perhaps not immediately obvious.[3] In contrast to a previous study,[4] we focus on the areas of the terraces. We claim that a sensible order parameter is the difference between the area of all the *A* terraces and the area of all the *B* terraces (normalized by the total area of all the terraces). This is a scalar (one-dimensional) order parameter, in which the system at every site of a two-dimensional lattice is given an "either-or" choice (viz. *A* or *B*), so that in the simplest picture, the transition, if continuous, should be in the Ising universality class.[5,6] (Complications, however, are conceivable.[7])

To substantiate this idea, we computed the square of this order parameter, as a function of temperature, for the terrace-step-kink (TSK) model of a vicinal surface. (The

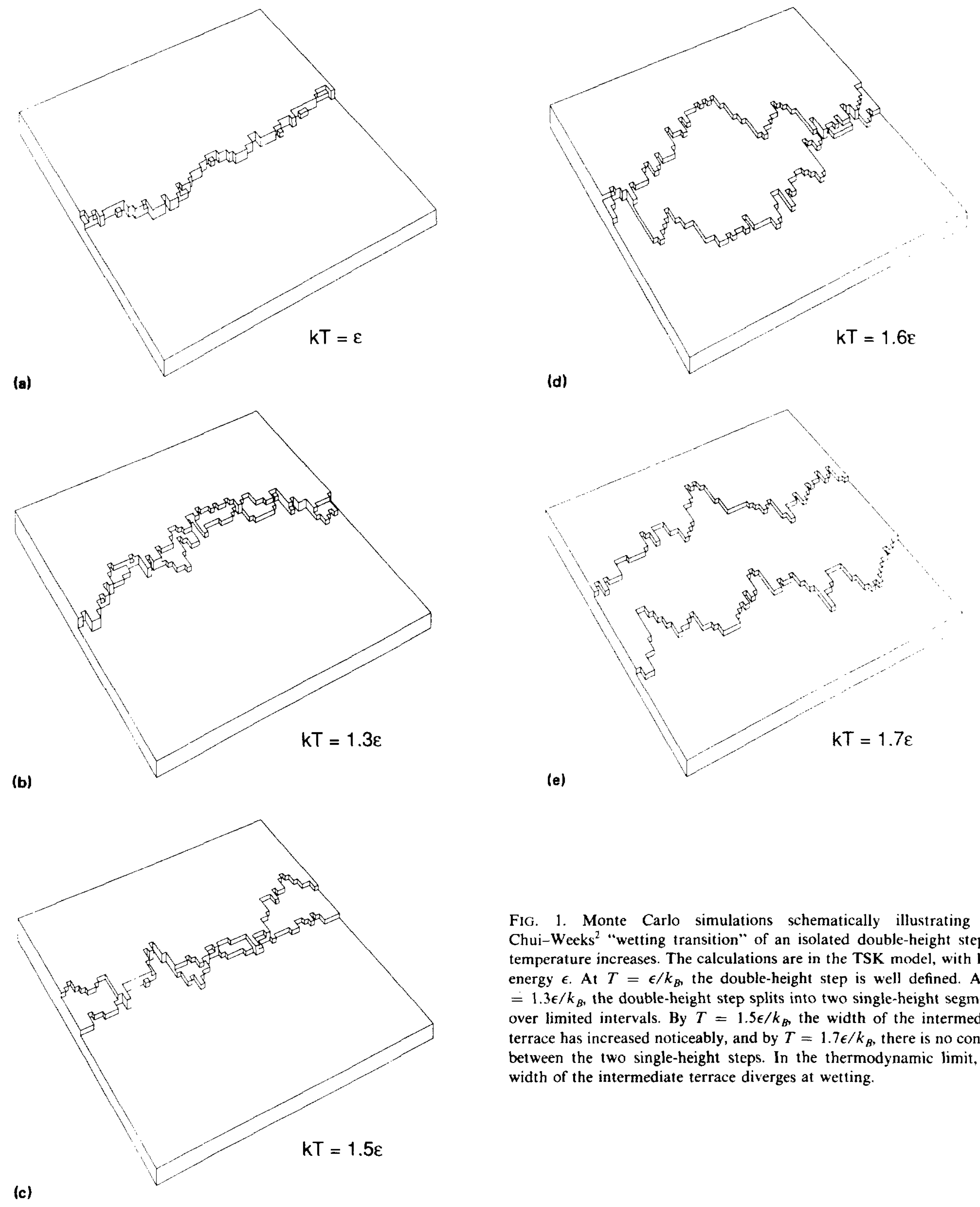

FIG. 1. Monte Carlo simulations schematically illustrating the Chui–Weeks[2] "wetting transition" of an isolated double-height step as temperature increases. The calculations are in the TSK model, with kink energy $\epsilon$. At $T = \epsilon/k_B$, the double-height step is well defined. At $T = 1.3\epsilon/k_B$, the double-height step splits into two single-height segments over limited intervals. By $T = 1.5\epsilon/k_B$, the width of the intermediate terrace has increased noticeably, and by $T = 1.7\epsilon/k_B$, there is no contact between the two single-height steps. In the thermodynamic limit, the width of the intermediate terrace diverges at wetting.

TSK model assumes that the only thermal excitation is wandering of the step edges; defects on or below the terrace plane are excluded. The approximation is quite adequate well below the roughening transition of the flat surface.) In a diffraction experiment, this squared order parameter is proportional to the intensity of the specular beam at an out-of-phase condition, at least in the kinematic limit. (The critical behavior, to leading order, should not be affected by multiple scattering.[8]) The results are depicted in Fig. 3, for several lattice sizes. As this size increases, the transition becomes sharper, as expected for a second-order phase transition and reminiscent of the intensity of "extra" spots induced by ordered overlayers in cases of continuous disordering. Instead of simple fits to power-law forms, experience in critical phenomena has been that a more precise estimate of critical exponents can be achieved using finite-size scaling theory.[9] This theory embodies the idea that the only relevant length in the critical regime is the

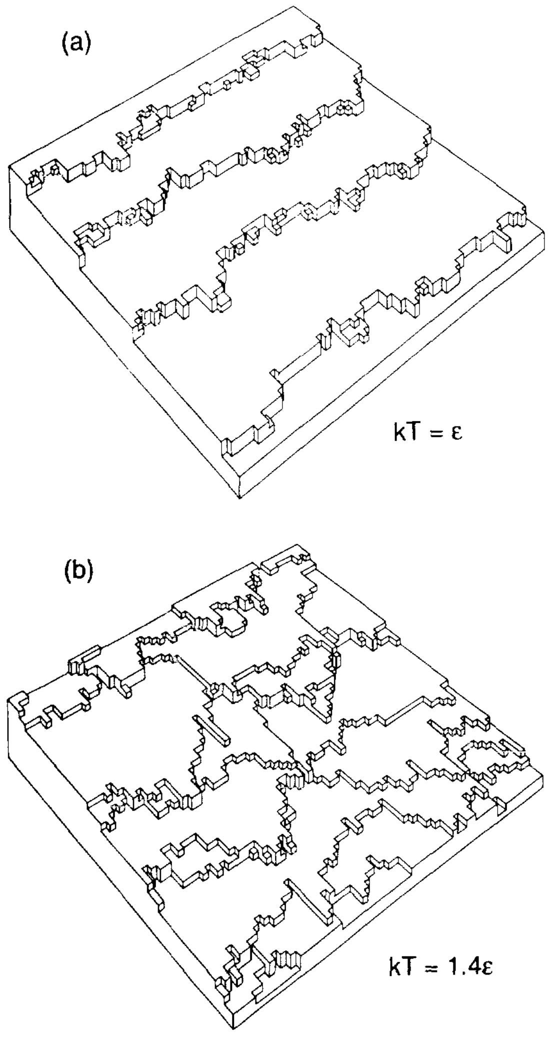

FIG. 2. Illustration of the transition occurring for a nondilute set of steps, again in the TSK model. Double-height steps predominate at low temperature (depicted here at $T = \epsilon/k_B$) while singles predominate at high temperature (here at $T = 1.4\epsilon/k_B$). In these Monte Carlo simulations, the energy per unit length of a single-height step equals that of a double-height step.

correlation length, and that finite size limits the growth of this length. In Fig. 4 we display such a log–log plot of the squared order parameter times $L^{2\beta/\nu}$ versus the reduced temperature $t = |1 - T/T_c|$ times $L^{1/\nu}$, using the Ising values $\beta = 1/8$ and $\nu = 1$. The data evidently scales well with these exponents, both above and below $T_c$. As an added test, we find that the slope of the former line, which should be $-\gamma$, is $-1.67 \pm 0.10$, consistent with the Ising model result $\gamma = 7/4$.

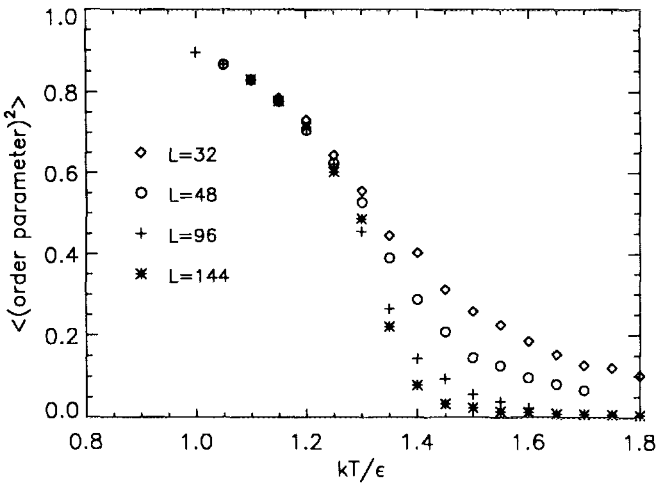

FIG. 3. Expectation value of the squared order parameter, i.e., the squared, normalized difference between the area of $A$ terraces and $B$ terraces, vs temperature, from Monte Carlo simulations of a terrace-step-kink model on an $L \times L$ lattice, for several $L$'s. The average terrace width was eight. The runs were $10^6$ Monte Carlo steps per site (MCS.) Temperature is in units of the kink energy in the TSK model.

To make the picture of this transition more complete, we now discuss the dependence on the misorientation angle $\theta$, or equivalently the average terrace width $l = 1/\tan(\theta)$. By performing finite-size analyses as in Fig. 4, we find that the [Ising] transition temperature decreases roughly linearly from the wetting temperature at the facet orientation. This behavior can be understood qualitatively based on the following argument: In the limit of isolated steps, below the wetting temperature $T_w$, adjacent bound single-height steps wander from each other with a characteristic width $l_w$, which is known[10] to have the form $a(T_w - T)^{-1}$, where $a$ is a proportionality constant. When $l_w$ becomes comparable to $l$, the steps are no longer isolated, but will encounter the presence of neighbors. Thus, we expect crossover to the Ising transition at $T_c^{\mathrm{Ising}}$ when $l = a(T_w - T_c^{\mathrm{Ising}})^{-1}$ [with $a$ model dependent], i.e.

$$T_c^{\mathrm{Ising}} \approx T_w - a/l. \qquad (1)$$

In Fig. 5 we show how well this equation describes the $T_c$'s extracted from Monte Carlo simulations at four values of the average terrace width.

In an earlier publication[11] some of us reported an evident physical realization of this transition on vicinal

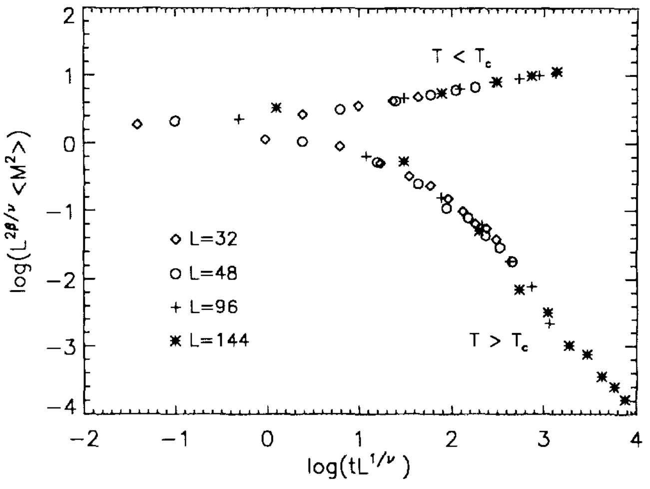

FIG. 4. Finite-size analysis of the simulated data in Fig. 3. The reduced temperature $t$ is $|1 - T/T_c|$. As illustrated, with the correctly chosen critical exponents and transition temperature, the data for different $L$ and $T$ collapse onto a single curve when plotted in the scaled fashion indicated on the axes.

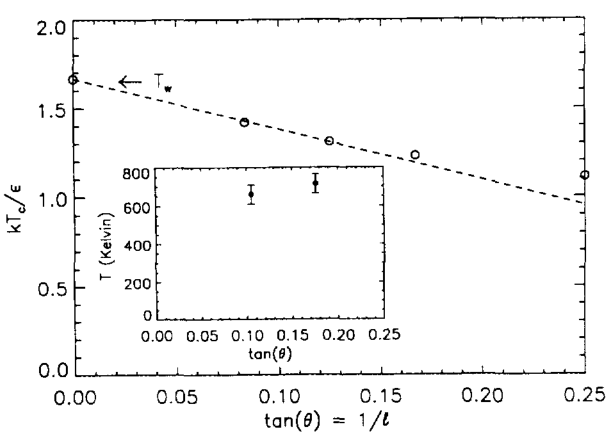

FIG. 5. $T_c$ vs misorientation angle for a simple TSK model of step doubling. The dashed line illustrates the linear decrease predicted by Eq. (1). The inset shows experimental data for Ge(111)-[1$\bar{2}$1]; evidently there is no decrease in $T_c$ with increasing misorientation angle.

Ge(111) misoriented (by 6° and 10°) toward the [1$\bar{2}$1] direction. This transition is observed by the emergence, as temperature is lowered, of specular LEED intensity at an out-of-phase energy for single-height steps. The reversible transition occurs about 100 K above the temperature at which the $c(2\times8)$ reconstruction disorders [to a weak $(2\times2)$], and so apparently is unrelated to that transition [in contrast, for example, to the first-order step-bunching transition of vicinal Si(111), which is driven by the $(7\times7)$ reconstruction[12]]. Attempts to fit limited measurements of the peak intensity of the specular beam to the form $A(T_c - T)^{2\beta}$ were thwarted by Debye–Waller effects. No convincing evidence of critical broadening was observed with our low-resolution instrument. However, indication that the transition is Ising-like has been obtained by measurement of the integrated intensity of the specular beam. In the neighborhood of the transition, this quantity has an energy-like anomaly[13]

$$I(T) \sim A_0 - B_\pm t^{1-\alpha}\,\mathrm{sgn}(T-T_c) - A_1(T-T_c). \quad (2)$$

Examples of fits to this form are displayed in Fig. 6. The value of the deduced specific heat exponent $\alpha$ is less than about 0.02, so consistent with the Ising value of 0 (i.e., logarithmic divergence). Moreover, the ratio of the critical amplitudes above and below $T_c$, $B_+/B_-$, is about 0.99, very close to the expected value of unity. Thus, there is evidence that the transition has Ising character.[14]

There are two other aspects of vicinal Ge(111) that are not explained in the simple theoretical picture: In the inset of Fig. 5 we show the $T_c$'s for samples misoriented by 6° and 10°. Evidently the transition temperature increases (or possibly is flat) as the misorientation angle increases, contrary to expectations based on crossover to Ising from wetting described above. Second, as one heats Ge through the transition, a well defined splitting appears as the specular beam fades. In our simulation of the simple TSK model, there are no noticeable split maxima appearing in this thermal range. Presumably longer range interactions than included in TSK are significant.

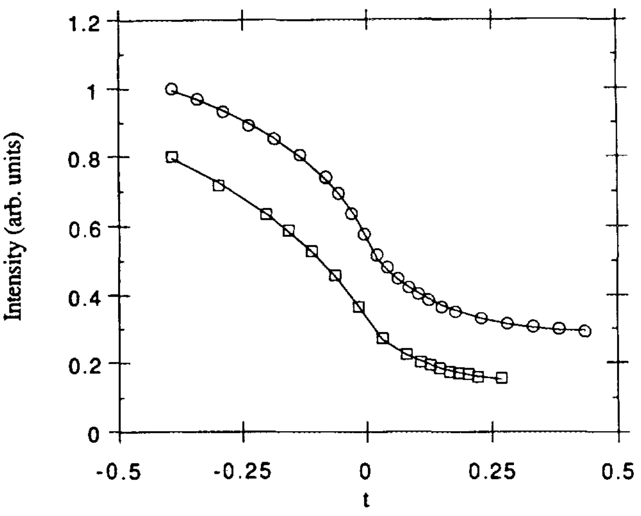

FIG. 6. Integrated specular beam intensities at an out-of-phase condition vs reduced temperature $t \equiv (T - T_c)/T_c$ for Ge(111) misoriented by 6° (○, upper data) and by 10° (□, lower) toward the [1$\bar{2}$1] direction. Since the units on the ordinate are arbitrary, the two sets of data are simply displaced from each other for clarity. The solid curves are the best fits to Eq. (2).

## III. STEP-DOUBLING WITHOUT SPONTANEOUS SYMMETRY BREAKING

In a distinctively different picture, single steps can be favored energetically at small misorientation; strong moderate-range repulsions then might lead to step doubling as misorientation angle increases. Note the important distinction from the previous scenario, in which long-range energetic interactions between steps were not at all necessary.

In recent years the case of vicinal reconstructed Si(001) misoriented toward the [110] direction has attracted great interest.[15] For this system the small-misorientation regime features single-height steps and terraces with both $(2\times1)$ and $(1\times2)$ reconstructions. (Going "downhill" from the $(1\times2)$ to the $(2\times1)$, one traverses nearly straight, high-kink-energy SA step; the other kind of step SB is highly meandering.) For misorientations greater than about 4°, adjacent single-height steps tend to coalesce into one of the two possible types of double-height steps DB separating $(2\times1)$ terraces, with dimer pairing along the mean step-edge direction and so dimer rows perpendicular to the step-edge direction. We emphasize that there is always more $(2\times1)$ area than $(1\times2)$, but that this preponderance increases substantially when the DB steps are plentiful.[3] In short, there is no symmetry breaking: the areas of $(2\times1)$ and of $(1\times2)$ are never the same, and the latter never predominates. Thus, there is no need to have a phase transition as misorientation angle increases; the relative fraction of $(2\times1)$ can just increase smoothly [without any singularity in its derivative]. If the energetics are such that a phase transition does occur, only local properties of the two phases need be different, and one would expect the transition to be first order.[16,17] Such a transition appears as a coexistence region in a phase diagram of temperature versus misorientation angle, since the latter (specifically, its tangent[18]) corresponds to a thermodynamic density. Surfaces prepared with angles within the coexistence region would break up into surfaces with stable orientations. Alternatively, in the equilibrium crystal shape, a "sharp edge" joins the two coexisting orientations, with all intermediate orientations absent; such behavior was reported by Umbach *et al.*,[19] albeit for a surface with a relatively large local curvature. No faceting, however, has been observed in the many scanning tunneling microscopy (STM) and LEED studies of these surfaces. (Ref. 17 has been widely misinterpreted as *predicting* the presence of a coexistence region for Si(001)-[110]; the intended theme of that Comment was merely that if a phase transition exists, as suggested by Ref. 16, it should be first order and so manifested by a coexistence region.)

We now comment on some specific models which have been proposed recently to account for the behavior of this vicinal surface. [In each case, our comments apply to the model *per se* rather than to the actual physical system.] Several models consider just a single pair of SB and SA steps, with periodic boundary conditions to reproduce the given average spacing (i.e., the miscut). This viewpoint is reminiscent of the Gruber–Mullins[20] approximation, in which a single active step is allowed to meander between two fixed straight steps separated by twice the mean step separation. In order to reproduce a phase transition, a many-body collective phenomenon, one must allow all steps to wander. Indeed, experimentally derived distributions of the SA–SA separations are not at all sharp, but are comparable in width to SA–SB distributions.[21] The best a single-step picture can do regarding transitions is to produce a [finite-size rounded] wetting transition such as discussed for Ge(111). Step-doubling transitions are implicitly but intrinsically excluded by this sort of model. First-order transitions are smeared out, so that they appear to be continuous transitions or no transitions at all. On the other hand, if there really is no transition, this viewpoint can be expected to give a good accounting of behavior.

An important ingredient in describing this physics is the relative magnitude of interactions between like steps (i.e., between singles or between doubles) compared to those between singles and doubles. When the latter are relatively small, Pehlke and Tersoff[22] show, in a simplified model that allows lone singles between doubles , that a subtle sequence of mixed phases, reminiscent of a devil's staircase, can replace the coexistence regime at zero temperature. At finite temperatures this behavior is presumably smoothed in some subtle way which would be difficult to predict.[23,24] Experimentally or in simulations, it would be quite a challenge to distinguish between a dense sequence of very weak first-order transitions and a continuous crossover as misorientation angle increases. (The mixed phases, however, can have very distinctive signatures in diffraction experiments—effects which have been observed, for example, in high-resolution electron diffraction studies of vicinal Si(111).[25]) Theoretical analysis, particularly in conjunction with numerical work, is confounded by the long-range interactions between steps. Moreover, the actual magnitude of the relevant interactions is not entirely clear for Si(001). [In the cases of vicinal Si(111) (toward $[\bar{2}11]$ or $[\bar{1}10]$)[12] and vicinal Ag(110),[26] in contrast, a coexistence region is clearly observed.] In the analysis of their full model, Pehlke and Tersoff claim that no transition is seen in some experiments because the temperatures at which mobility is sufficient to permit equilibration may lie above the critical temperature capping the mixed phase region; this viewpoint, as they state, has not been established compellingly from first-principles calculations.

Finally, the issue has been raised[3] whether the Chui–Weeks analogy[2] sheds light on vicinal Si(001). As suggested by the discussion in the previous section, this model might well describe the separation of an isolated DB step into SA and SB steps, if an isolated DB step were ever stable, contrary to experimental evidence. Since step interactions are crucial for the Si(001) problem, one is in the regime in which the perpendicular fluctuations of the DB step (or its SA and SB constituents) are significantly restricted. In the symmetric case of the previous section, this limitation led in our simple picture to crossover to Ising behavior. Here we suspect it completely destroys the phase transition.

## IV. HIGHER-MULTIPLICITY TRANSITIONS

For step tripling transitions, we extend the previous viewpoint by designating terraces separated by single-height steps as *A*, *B*, and *C*, in repetitious sequence. Above the transition, one expects comparable area for all three while below, one of the three predominates. To construct an order parameter, we can take

$$\frac{(\text{area A}) + \exp(i\pi/3)(\text{area B}) + \exp(i2\pi/3)(\text{area C})}{\text{total area}}. \tag{3}$$

This has the form of a three-state Potts model, actually a [highly] chiral three-state Potts model since there are AB and BC steps but no BA or CB steps (or vice versa). Experimentally, the square of this order parameter can be monitored by measuring the specular intensity using an incident energy such that the normal component of the scattering wave vector introduces a phase of $\exp(i\pi/3)$ or $\exp(i2\pi/3)$ between adjacent layers. While the exponents of this model are usually found to be close to those of a nonchiral three-state Potts model, the ratio of the critical amplitudes that one might measure for the integrated intensity (cf. Fig. 6) should be different, i.e., not unity.[10,27]

The only physical instance of step tripling of which we are aware occurs on Si(111) misoriented toward the $[\bar{1}\bar{1}2]$ direction.[25] The onset of this tripling with increasing misorientation angle occurs by way of a mixed phase reminiscent of the Pehlke–Tersoff simple model, rather than a coexistence region of a single-height-dominated phase and triple-height-dominated phase or a critical onset. Thus, we find neither a chiral three-state Potts model nor a simple first-order transition, but rather some complicated behavior.

For higher-order coalescence, the order parameter will have even higher dimensionality. Usually the transitions involving such order parameters are found to be first order.

In closing, we hope these remarks show the importance of identifying whether symmetry is broken in any phase transition and using this scrutiny to set down a sensible order parameter. Furthermore, it highlights the idea that when symmetry is not broken, one can go from one regime to another smoothly, without any phase transition.

## ACKNOWLEDGMENTS

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