Roughening-Induced Deconstruction in (110) Facets of fcc Crystals

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A chiral four-state clock-step model is introduced to describe the deconstruction and roughening of missing-row-reconstructed (110) facets of fcc crystals. Unlike simple cubic (110) facets, a reconstructed rough phase is absent. Roughening induces a simultaneous deconstruction transition, which at zero chirality has central charge $c=1.5$ and both Ising and conventional roughening critical exponents. Pt(110) and Au(110) are suggested as realizations of this at small chirality, where this transition has the character of an incommensurate melting transition into a rough incommensurate missing-row fluid.

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The interplay between surface reconstruction and roughening leads to intriguing new types of critical phenomena. For unreconstructed surfaces it gives rise to preroughening transitions[1,2] and for reconstructed surfaces to the roughening-induced deconstruction phase transition described in this paper. Recent experimental evidence suggests that Ni(110) and also Ar(111) are possible realizations of preroughening.[2-5] The missing-row- (MR-) reconstructed (110) facets of Pt(110) and Au(110) are being studied extensively.[6-9] At first the possible coupling between surface roughening and deconstruction was overlooked, and the transition was believed to be simply Ising-like.[6] Villain and Vilfan[8] pointed out that surface roughening should be expected to play a role. Indeed, the most recent experimental results for Pt(110) indicate the presence of step excitations.[9]

First, let me point out a fundamental difference between MR reconstruction in simple-cubic (sc) and face-centered-cubic (fcc) (110) facets: Fig. 1 versus Fig. 2. The MR order in Fig. 1(a) can be characterized by an angle variable, $\theta=\pi n_t$, representing the two possible positions of the top rows, $n_t=1,2(\mathrm{mod}2)$. Consider wall and step excitations. Walls, see Fig. 1(b), do not change the surface height, $dh=0$, but couple to the reconstruction, $d\theta=\pi$. They have a topological charge $(d\theta,dh)=(\pi,0)$. Surfaces where walls are more favorable than steps, $R=E_w/E_s<1$, deconstruct first and only roughen later. Steps, see Fig. 1(c), have a topological charge $(d\theta,dh)=(\pi,\pm 1)$. This suggests that steps couple to both order parameters, and that surfaces with $R>1$ roughen and deconstruct simultaneously. This is not so. We can disentangle the order parameters by switching the two MR labels after each step, $\theta\rightarrow\theta+\pi$. A better way is to represent the MR order by parity; define Ising spins as $S_r=\exp(i\pi h_r)$. Figure 1(c) illustrates that the antiferromagnetic spin order persists across steps, and that steps do not couple to the MR order. A sc (110) facet with $R>1$ roughens first, and then enters a reconstructed rough phase, followed by an Ising deconstruction transition at a higher temperature (T). The restricted solid-on-solid (RSOS) model shows this type of

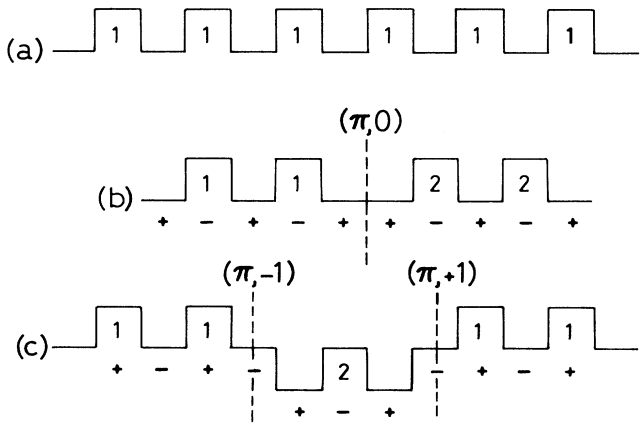

FIG. 1. (a) Missing-row-reconstructed simple-cubic (110) facet, (b) with a wall excitation, and (c) with two steps.

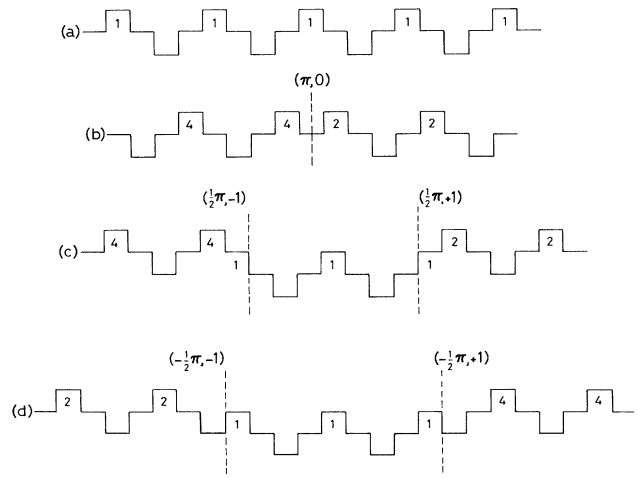

FIG. 2. (a) Missing-row-reconstructed face-centered-cubic (110) facet, with (b) a wall, (c) two clockwise steps, and (d) two anticlockwise steps.

behavior;[1,2] it describes checkerboard-reconstructed sc (100) facets.

The (110) facets of fcc crystals, e.g., Pt(110) and Au(110), have an anisotropic body-centered-type structure. Atoms in adjacent layers are not located on top of each other, but on top of the plaquettes. This MR order, see Fig. 2(a), is characterized by an angle variable $\theta = \frac{1}{2}\pi n_t$, representing the four possible positions of the top rows, $n_t = 1,2,3,4 (\mathrm{mod} 4)$. The MR state is twofold degenerate because at a specific surface height only $\theta = 0, \pi$ or only $\theta = \pm \frac{1}{2}\pi$ can be realized. Again we can distinguish between walls and steps,[8] see Figs. 2(b)–2(d), and identify their topological charge $(d\theta, dh)$. At every $d\theta = \pm \frac{1}{2}\pi$ type domain wall the height change is odd (the steps). At every $d\theta = \pi$ type domain wall the height change is even (including the walls with $dh = 0$). From Fig. 2 it will be clear that it is impossible to redefine the θ variables such that steps do not couple to the θ's. The MR and roughening order parameters cannot be disentangled. fcc (110) facets with $R > 2$ behave differently from their sc counterparts; roughening induces a simultaneous deconstruction transition.

This absence of a reconstructed rough phase in fcc (110) facets poses the question about the nature of the transition. Earlier experimental results for Au(110) have been interpreted in terms of $R < 2$, since Ising-type critical exponents are observed.[6] But we will see that the roughening-induced deconstruction transition at $R > 2$ has Ising-type exponents too.

It is possible to model fcc (110) facets by an anisotropic body-centered SOS model, but the required interaction range makes this model not very palatable to a numerical finite-size-scaling (FSS) study. In the MR structure the top layers are compressed and buckled.[7] Therefore the microscopic domain-wall structures will be less sharp than shown in Fig. 2. They might have a width l_w of up to several unit cells, similar to domain walls in physisorbed monolayers.[10] This relaxation does not affect the topological charge, nor the nature of the phase transition. Domain walls can exchange charge at intersections and dislocations, but the total charge is preserved. These merging rules, together with R, determine the universality class of the phase transition.[10] Also the observed shift in diffraction peaks[9] reflects only the charge,[10] not the internal structure of the domain walls.[11] The peak shift indicates the appearance of an incommensurate (IC) MR (fluid) structure similar to those in adsorbed monolayers.[10] The shift reflects the lateral translation of the MR unit cell between domains at opposite sides of a step.

Consider the following cell-spin model. Imagine a rectangular lattice oriented along the grooves of the missing rows. Each cell, i.e., the unit cell of this lattice, is large compared to the MR unit cell, at least of order l_w, but small compared to the correlation length (which is large close to T_c). Fluctuations at length scales smaller than l_w are integrated out. Associate with each cell a $\theta_{n,m} = 0, \pm \frac{1}{2}\pi, \pi$ variable, to represent the four MR states. Consider the partition function

$$Z = \sum_{\{\theta_{n,m}\}} \exp\Big\{ \sum_{n,m} [K_m \cos(\theta_{n,m} - \theta_{n,m+1} - \Delta) + Q_m \cos(2\theta_{n,m} - 2\theta_{n,m+1}) + K_n \cos(\theta_{n,m} - \theta_{n+1,m}) + Q_n \cos(2\theta_{n,m} - 2\theta_{n+1,m})] \Big\} Z_{6V}(\{d\theta = \pm \tfrac{1}{2}\pi\}, L) . \quad (1)$$

This is a four-state clock model, with chiral-symmetry breaking, Δ. Every configuration is weighted by a six-vertex (6V) model. The walls and steps follow the bonds of the lattice. The θ variables describe their position and also the MR aspect of their topological charge. In a 6V model arrows are placed on the bonds of a lattice such that the flux of arrows is zero at all vertices. In Eq. (1) this lattice is not fixed, but is the annealed fluctuating lattice, formed by the $d\theta = \pm \frac{1}{2}\pi$ domain walls of the clock model (the $d\theta = \pi$ walls do not change the height). The 6V arrows represent the change in height at the steps (similar as in Ref. 1). K_m, Q_m, and Δ represent the step and wall energies. These depend only on $d\theta$, because the structure of up and down steps, $dh = \pm 1$, is the same, the left-right symmetry in Figs. 2(c) and 2(d). Δ represents the energy difference between clockwise, $d\theta = \frac{1}{2}\pi$, and anticlockwise, $d\theta = -\frac{1}{2}\pi$, steps. K_n and Q_n represent the energies of kinks. Steps and walls will interact; L is an example of a step-step interaction that favors up-down step order. I believe that Eq. (1) contains all interactions essential for the nature of the phase transition.

Chiral clock models without these novel height degrees of freedom are familiar from the theory of IC adsorbed monolayers. As in those models,[10] a fermion-type analysis is possible in the strong-chirality limit. Villain and co-workers[3] proposed a theory for Pt(110) which is equivalent to this limit. It leads to the exactly soluble one-dimensional Hubbard model. The fermions represent the $(d\theta, dh) = (\frac{1}{2}\pi, \pm 1)$ steps, and their spin the step height $dh = \pm 1$. The $(d\theta, dh) = (\pi, 0)$ walls are viewed as bound states of fermions with antiparallel steps. The anticlockwise steps are frozen-out Δ couples to the chemical potential of fermions. Villain and coworkers find a Pokrovsky-Talapov- (PT-) type transition where the surface roughens and deconstructs simultaneously. This deconstruction is only partial, however; the θ

variables retain IC-floating-solid-type order. Dislocations must be added to the fermion Hamiltonian, i.e., that quartets of fermions with total spin zero can annihilate and create each other,[10] to describe the melting of the MR order.

I chose to focus on the small-Δ limit. This is the theoretically most interesting limit. Moreover, the observed small peak shift in Pt(110) suggests a small Δ. I studied numerically the FSS behavior of semi-infinite strips. The details will be presented elsewhere. I chose $L=0$ and isotropic interactions $K_n=K_m$ and $Q_n=Q_m$. Since the maximum accessible strip width is quite small, $N\leq 7$, the results are not as conclusive as in similar FSS studies for models with less degrees of freedom per bond. Consider (ϕ,k)-type boundary conditions, with $\theta(n+N,m)=\theta(n,m)+\phi$ and $h(n+N,m)=h(n,m)+k$, and calculate the free-energy differences, $\eta(\phi,k)=N[f(\phi,k)-f(0,0)]$. These boundary conditions force specific walls and steps into the system. The vanishing of $\eta(\pi,0)$ indicates the disappearance of the MR order. The vanishing of $\eta(0,2)$ indicates surface roughening. $\eta(\pi,1)$ represents the free energy of a step.

Figure 3 shows the phase diagram at $\Delta=0$. At small R, where walls are more favorable, $\eta(\pi,0)$ vanishes first. The location of the deconstruction line follows from the crossing points where the $N\eta(\pi,0)$ curves at successive values of N cross. $\eta(\pi,0)$ scales with the correct Ising universal FSS amplitude. $\eta(\frac{1}{2}\pi,1)$ and $\eta(0,2)$ vanish at a higher T. In the rough phase they scale as power laws: $N\eta(\frac{1}{2}\pi,1)=\frac{1}{2}K_G$ and $N\eta(0,2)=2K_G$, with K_G the roughness parameter.[1] The location of the roughening line follows from the condition $N\eta(0,2)=\pi$, using the fact that $K_G=\frac{1}{2}\pi$ at a Kosterlitz-Thouless (KT) transition.

The Ising and KT line meet and merge at $R=2.0\pm 0.1$. At first I expected the transition at $R>2$ to be first order: But it is not. Ising and roughening critical behavior seem to be superimposed. The condition $N\eta(0,2)=\pi$ and the crossing points of $N\eta(\pi,0)$ and $N\eta(\frac{1}{2}\pi,1)$ converge to the same estimate for the critical line. At its crossing points $\eta(\pi,0)$ scales as $N\eta(\pi,0)=0.81\pm 0.03$, consistent with the Ising value $2\pi x_H$ (with $x_H=\beta/y_T=\frac{1}{8}$). A power-law fit to the temperature derivative, $d(N\eta)/(dT)\simeq N^{y_T}$, gives the Ising-type value $y_T=1.0\pm 0.1$ for all three η's. The central charge c follows from the FSS scaling of $f(0,0)$. The location of the maxima of c scales with N towards again the same critical-line estimate. The value of c at these maxima converges to $c=1.50\pm 0.05$ along the entire line. The step free energy $\eta(\frac{1}{2}\pi,1)$ has a surprising universal amplitude, $N\eta(\frac{1}{2}\pi,1)=1.03\pm 0.03$ (corrections to scaling in this quantity are virtually absent).

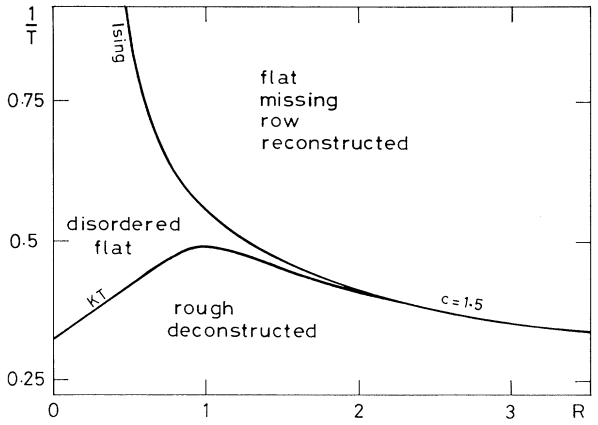

FIG. 3. Phase diagram of the four-state chiral clock-step model, at zero chirality ($\Delta=0$), with $R=E_w/E_s$, and temperature T in units of E_s.

Rewrite each θ variable in terms of two coupled Ising spins; $\theta=0,\frac{1}{2}\pi,\pi,\frac{3}{2}\pi$ as $(S,T)=(++),(+,-),(-,-),(-,+)$. The 6V arrows are located on the bonds of the joint lattice formed by the Bloch walls of both Ising models, but bonds where their Bloch walls overlap are excluded. Redefine the spins such that the 6V model arrows sit on the Bloch walls of one Ising model only. This can be achieved in two ways: define $\sigma=ST$ and keep S or keep T; I call this S-T invariance. Next, the σ spins and 6V arrows can be combined into height variables $h_{\mathbf{r}}$ of a RSOS model, as $\sigma=\exp(i\pi h)$, like in Ref. 1. Therefore, Eq. (1) is equivalent (at $\Delta=0$) to an Ising model coupled to an RSOS model,

$$Z=\sum_{\{h_{\mathbf{r}},T_{\mathbf{r}}\}}\exp\left(\sum_{\langle\mathbf{r},\mathbf{r}'\rangle}\{\tfrac{1}{2}K_I T_{\mathbf{r}}T_{\mathbf{r}'}+(\tfrac{1}{2}K_S T_{\mathbf{r}}T_{\mathbf{r}'}+Q)[1-2(h_{\mathbf{r}}-h_{\mathbf{r}'})^2]\}\right), \tag{2}$$

with $K_S=K_I=K$, and for simplicity $L=0$. A duality transformation on the RSOS degrees of freedom maps Eq. (2) into an XY model coupled to an Ising model. This is essentially the same model studied in recent years in the context of the fully frustrated XY model.[12] Monte Carlo results for these models are consistent with my numerical results.

A central charge $c=\frac{3}{2}$ is associated with conformal field theories with supersymmetry,[12] invariance under a continuous transformation that mixes massless fermion and boson degrees of freedom. An example of this is the Ising deconstruction critical point inside the rough phase of sc (110) facets.[1,2] Another example is the $K_S=0$ limit of Eq. (2) where the Ising and roughening degrees of freedom decouple. Supersymmetry holds only asymptotically at the Ising critical points in the rough phase. Also, it does not impose a connection between the Ising and roughening T_c's, since the $h_{\mathbf{r}}$ behave in the rough phase as nondiscrete variables, whose magnitudes can be

rescaled freely. So, a reconstructed rough phase exists at $K_s=0$. It persists at small values of K_s, because at $K_s=0$ the K_s interaction has an irrelevant scaling index, $y_{K_s}=3$. S-T symmetry implies the same behavior in the opposite, $K_t=0$, limit. Our model at $K_s=K_t$ is the separatrix between these two regions.

S-T invariance implies that $K_s=K_t$. It represents our inability to disentangle the roughening and MR degrees of freedom. S-T invariance has the character of a fermion-boson exchange too. On the one hand it is weaker, only a discrete Z_2-type invariance. On the other hand it is stronger, an exact invariance of the model that holds also away from criticality. It imposes the link between the roughening and deconstruction that requires the two transitions to coincide.

In Pt(110) and Au(110), the clockwise and anticlockwise steps have different energy, $E_{cs}=(1-D)E_s$ vs $E_{as}=(1+D)E_s$. Assume that for small D at $R>2$ the phase diagrams of Eq. (1) and the conventional chiral three-state clock model[10] look alike: an IC melting transition at small D, and a Lifshitz point, at an intermediate value of D, where the critical line splits into a PT and KT line with a (rough) IC (MR) floating solid phase in between (the fermion description mentioned above).

I suggest that Pt(110) and Au(110) are realizations of this IC melting transition at small D. The surface simultaneously roughens and undergoes a IC-melting-type deconstruction transition with respect to the MR degrees of freedom. The rough IC MR fluid phase contains more clockwise than anticlockwise steps. This causes the shift Q in the liquidlike half-order diffraction peaks. Compared to the correlation length ξ, Q vanishes at T_c as $Q\sim\xi^{-x_Q}$. If $x_Q>1$, all critical exponents must remain the same as at $D=0$.[10] This is not evident for $x_Q=1$, but numerical evidence for the chiral three-state clock model supports $x_Q=1$ and no change in the exponents.[10] Assume that also in our case $x_Q=1$, and that all critical exponents are the same as at $D=0$. This implies a linear vanishing of the misfit $Q\sim|T-T_c|^{x_Q/y_T}\sim|T-T_c|$. This is remarkably consistent with the observations for Pt(110). Robinson *et al.*[9] find that the intensity of the half-order peak scales as $|T-T_c|^{2\beta}$ with $\beta\simeq0.11$ and the peak width as $\xi^{-1}\sim|T-T_c|^{y_T}$ with $y_T\simeq1.05$, both consistent with my values at $D=0$, and they observe a linear vanishing of the misfit.

In my FSS calculation, the pitch appears as the complex part of the next-leading eigenvalue λ_1 for periodic boundary conditions, $m+iQ=\ln(\lambda_0/\lambda_1)$. m is proportional to the peak width in the rough IC fluid phase and vanishes in the MR phase. At $(R,D)=(3,\frac{1}{4})$, the crossing points of $\eta(\pi,0)$ and $\eta(\frac{1}{2}\pi,1)$ converge to a higher estimate for T_c than the crossing points of m. This indicates that we have passed the Lifshitz point. At $(R,D)=(1,\frac{1}{8})$, the crossing points of Nm and the $N\eta$'s give the same T_c within the numerical accuracy (2%).

In Pt(110), Q saturates at $\epsilon_0=(T_0-T_c)/T_c=0.06$ at $Q=0.03$ reciprocal-lattice units, and for $\epsilon<\epsilon_0$ the correlation length is smaller but of the same order of magnitude as the wavelength of the IC fluid, $\xi^{-1}\sim m\simeq2Q\simeq\epsilon$.[9] In my model Q takes a similarly small value at $(R,D)=(3,\frac{1}{8})$. Assuming a single transition, I find that the temperature derivatives of m, $\eta(\pi,0)$, and $\eta(\frac{1}{2}\pi,1)$ scale with an exponent $y_T\simeq0.95\pm0.5$. The pitch Q scales at the crossing points of m consistent with a valence $x_Q=1$, but not fully convincingly. This should be expected. The wavelength in the IC fluid is large (set at small N by pseudo-one-dimensional behavior), while ξ is limited by the strip width as $\xi\leq N$. At $N=7$ these two length scales just barely start to compete.

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