Anisotropic Phase Transition on Uniaxial Surfaces

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A centered rectangular lattice-gas model for the chemisorption of H on Fe(110) is studied by transfer-matrix scaling. The results indicate a new type of phase transition to a uniaxial modulated "(3×1)" phase with anisotropic critical behavior.

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Monolayers of atoms adsorbed on surfaces often undergo a continuous transition to a phase with broken substrate symmetry. In several cases the nature of such a transition can be predicted via a mapping of an effective Hamiltonian derived from Landau symmetry rules to well-known Ising, Potts, or vector models.[1] Thus a transition to a uniaxial commensurate $p\times 1$ structure is predicted to be Ising-like for $p=2$.[2] For $p>2$ the transition is expected to be in the universality class of vector Potts (clock) models,[3-5] sine-Gordon models,[6,7] or their quantum versions.[8,9] In these cases the $p\times 1$ structure may melt to an incommensurate floating phase with zero order parameter and algebraic decay of correlations which has a Kosterlitz-Thouless transition to the disordered high-temperature phase.[10]

Recently it was suggested[4] that for $p=3$, fluctuations characterized by light or heavy domain walls are important for the nature of the phase transition. Thus the phase diagram of a (3×1) structure, which for instance is observed for hydrogen adsorbed on a Fe(110) surface,[11] should have a line where "chirality" defined by the free-energy difference of light and heavy walls is zero. On this line the transition is predicted to be three-state Potts-like. Away from this point chirality is relevant[4,6] and may change the transition. However, the nature of the transition and the topology of the phase diagram are still controversial.[3-9]

All of the models mentioned above are related to the real monolayer transition via universality arguments only. However, in particular for chemisorbed atoms, lattice-gas models are expected to be a more microscopic and realistic description.[12] In fact, for H/Fe(110) a centered rectangular lattice-gas model with short-range pair and triple interactions gave a satisfactory description of the phase diagram and the structure factor[13] which experimentally were obtained by low-energy electron diffraction (LEED).[11]

In this Letter the nature of the (2×1) and (3×1) phases of this model are studied in more detail. The critical properties are calculated by transfer-matrix scaling (TS).[14] In particular the problem of anisotropic scaling is investigated. The results indicate the following:

(i) For coverages θ between $\theta\simeq 0.42$ and $\theta\simeq 0.54$ there is a (2×1) phase with an Ising transition and isotropic scaling.

(ii) For $0.54\lesssim\theta\lesssim 0.82$ there is another continuous transition to a "(3×1)" phase. At $\theta\simeq 0.69$ the line of zero chirality intersects the phase boundary. Only close to this point do I find isotropic scaling; otherwise there are two correlation lengths $\xi_{\parallel}$ and $\xi_{\perp}$ parallel and perpendicular to the rows of constant coverage which diverge with two different critical exponents $\nu_{\parallel}$ and $\nu_{\perp}$, respectively. The ratio $\nu_{\perp}/\nu_{\parallel}$ is smaller than 1 and varies with coverage θ.

(iii) For the (2×1) phase transition the wave vector φ of the critical correlations is locked in at $\varphi/2\pi=\frac{1}{2}$, whereas for the "(3×1)" phase φ seems to vary continuously from $\varphi/2\pi\simeq 0.3$ to $\varphi/2\pi\simeq\frac{1}{2}$ with decreasing coverage. For zero chirality, at $\theta\simeq 0.69$, one has $\varphi/2\pi=\frac{1}{3}$ corresponding to a commensurate (3×1) structure.

(iv) There is no indication of a floating phase; the correlation lengths $\xi_{\parallel}$ and $\xi_{\perp}$ of the "(3×1)" phase seem to grow exponentially with the system size as in a usual ordered phase.

(v) Whereas the (2×1) phase boundary can be determined from experiments on small surface patches, the "(3×1)" transition is drastically influenced by finite-size effects due to anisotropic scaling.

The results (ii) to (iv) are at variance with present theories.[3-10] This might be due to the fact that the present method has not yet revealed the true asymptotic behavior. However, experience with many other models rather suggests that there is a new kind of a phase transition with anisotropic scaling.

The results are obtained from finite-size scaling (or phenomenological renormalization) intro-

duced by Nightingale.[14] The correlation length $\xi_\perp$ of an infinite strip of finite width N is calculated exactly from the largest eigenvalues of a transfer matrix. The critical properties for $N\to\infty$ are obtained from the scaling assumption

$$\xi_\perp(t,N^{-1}) = b^{\nu_\perp/\nu_\parallel}\xi_\perp(b^{1/\nu_\perp}t, b/N), \quad (1)$$

where t is a distance from the critical line $T_c(\theta)$. Note that b is the rescaling factor for the strip width N, whereas $\xi_\perp$ is a length along the infinite direction, i.e., perpendicular to the rescaled length N. Therefore in general for anisotropic models one has to consider *anisotropic* scaling $\nu_\perp \neq \nu_\parallel$. However, renormalization methods close to four dimensions[15] and exactly solved two-dimensional anisotropic Ising models[16] show that in most cases the critical behavior is isotropic. Only in some special cases like Lifshitz points,[17] directed percolation,[18] commensurate-incommensurate transition,[8,10] and three-dimensional liquid crystals[19] has anisotropic scaling been observed.

In practice one takes $b = N/(N-1)$ and plots

$$Y_N = \ln\left(\frac{\xi_\perp(T,N)}{\xi_\perp(T,N-1)}\right)\left[\ln\left(\frac{N}{N-1}\right)\right]^{-1}$$

as a function of temperature T as shown in Fig. 1. In general,[14] in a disordered phase Y_N goes to zero with $N\to\infty$; in an ordered phase one has $Y_N \sim N$ showing an exponential increase of $\xi_\perp$ with N. At a critical point or in a floating phase one has for $N\to\infty$ $Y_N = \nu_\perp/\nu_\parallel$. Therefore the intersections of the different curves Y_N in Fig. 1 determine T_c and $\nu_\perp/\nu_\parallel$. The error made by using finite N values can be estimated from the N dependence of the results. It turns out that for many models rather small N values give good results.[14]

Here we study a centered rectangular lattice-gas model with Hamiltonian

$$\mathcal{H} = -J_2[R_1\textstyle\sum^1 S_iS_j + \sum^2 S_iS_j + R_3\sum^3 S_iS_j + R_t\sum^t S_iS_jS_k - hS_i], \quad (2)$$

where $\sum^\nu$ denotes the summation over (1) second-, (2) first-, and (3) third-neighbor pairs, and (t) the smallest triangles. $S_i = 1$ if an atom occupies site i and $S_i = -1$ otherwise. For details see Ref. 13. We use the coupling ratios $R_1 = -\frac{1}{2}$, $R_3 = \frac{1}{2}$, and $R_t = -\frac{1}{4}$ with repulsive $J_2 < 0$ which reproduce the experimental data of H/Fe(110)[11] reasonably well. The same transfer matrix of size $4^N \times 4^N$ as in Ref. 13 is used which gives the length $\xi_\perp$ and the wave vector φ of the asymptotic decay of correlations in the direction of the (2×1) or (3×1) modulation.

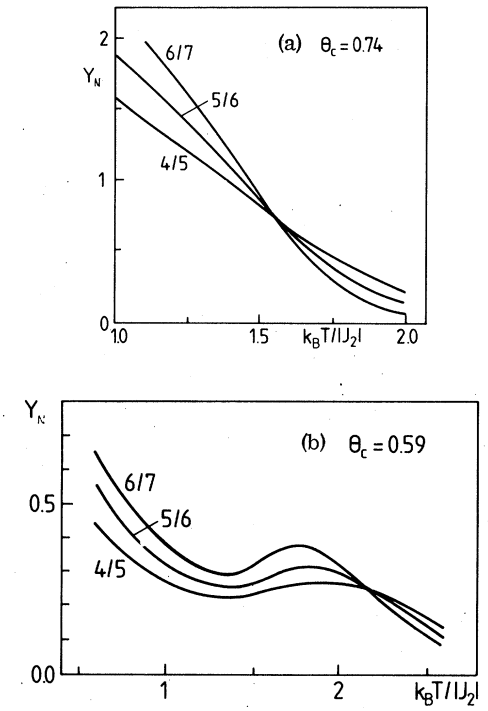

FIG. 1. $Y_N = \ln[\xi_\perp(T,N)/\xi_\perp(T,N-1)]\{\ln[N/(N-1)]\}^{-1}$ as a function of temperature for (a) $h = 4$ and (b) $h = 1.6$ and different $(N, N-1)$ values. θ_c is the coverage at the intersection point $(T_c, \nu_\perp/\nu_\parallel)$.

Figures 1(a) and 1(b) show two examples for Y_N as a function of temperature. Figure 1(a) looks like a usual phase transition except for the fact that the curves intersect at $Y \simeq 0.75$ instead of $Y = 1$. For the pairs of strip widths N which I was able to calculate, no strong N dependence is seen, and so the intersections do not seem to approach $Y = 1$ for $N\to\infty$. This means anisotropic scaling with $\nu_\parallel \neq \nu_\perp$.

Figure 1(b) shows $Y_N(T)$ for $h = 1.6$ close to the point $h = 1.5$ where the (2×1) and (3×1) structures are highly degenerate at zero temperature[13] and an incommensurate floating phase is expected.[3-6,9,10] The nonmonotonic behavior is a consequence of that fact that $\xi_\perp(T=0)$ is finite for $h = 1.5$ but infinite for $1.5 < h < 4.5$ where the (3×1) ground state is stable. Figure 1(b) indicates that $Y_N \sim N$ below the intersection point T_c. This would rule out the possibility of a floating phase where $Y_\infty = \lim_{N\to\infty} Y_N$ should be finite. Note that in other models, with use of the same N values, a floating phase can clearly be identified from $Y_\infty \simeq 1$, where Y_∞ is obtained from extrapolating Y_N to $N = \infty$ by a power law.[14,20]

Figure 2 shows $\nu_\perp/\nu_\parallel$ as a function of coverage

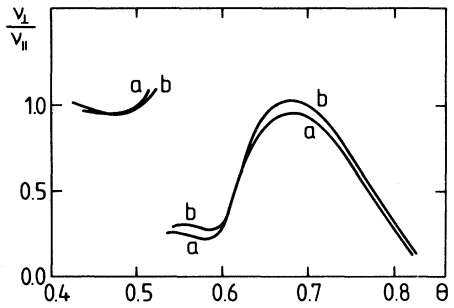

FIG. 2. Ratio of correlation-length exponents $\nu_\perp/\nu_\parallel$ as a function of coverage for the (2×1) and "(3×1)" phase boundaries at low and high coverages, respectively. Curves a and b are determined from strips with $N=(4,5,6)$ and $(5,6,7)$, respectively.

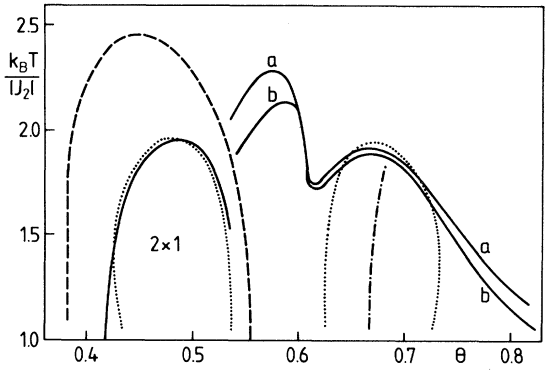

FIG. 3. The solid lines give the phase boundary in the temperature-coverage plane, derived from strips with (curve a) $N=(4,5,6)$ and (curve b) $N=(5,6,7)$ [for the (2×1) phase curves a and b cannot be distinguished in the figure]. The dashed line is the disorder line $T_D(\theta)$ for $N=5$. On the dash-dotted line chirality is zero. The dotted line shows the temperature T where $\xi_\perp(T, N=6)=6$.

determined from the intersections of $Y_N(T)$. For the transition to the (2×1) phase at low coverages the results are consistent with $\nu_\perp=\nu_\parallel$ in agreement with the expected Ising transition. However, for the transition to the "(3×1)" phase at high coverages, the ratio $\nu_\perp/\nu_\parallel$ varies strongly with coverage. Although I have not used enough strip widths N to account precisely for the corrections to scaling there is no indication that one gets isotropic behavior $\nu_\perp=\nu_\parallel$. The data do not quite rule out the possibility of an anisotropic transition with $\nu_\perp/\nu_\parallel<0.5$ being constant for $0.54\lesssim\theta\lesssim 0.61$, a multicritical point with $\nu_\perp/\nu_\parallel\simeq\frac{2}{3}$ at $\theta\simeq 0.61$, and an isotropic transition for $0.61\lesssim\theta\lesssim 0.73$. But for higher coverages the anisotropy $\nu_\perp/\nu_\parallel$ seems to vary continuously.

Figure 3 shows the critical temperature as a function of coverage. In contrast to Ref. 13 where isotropic scaling was assumed the "(3×1)" phase boundary extends over a broad coverage range. On the dash-dotted line the interface free energies of light and heavy walls which are determined exactly for $N=7$ are equal. Note that at the top of this line the transition is isotropic (see Fig. 2) in agreement with the predicted three-state Potts point for zero chirality.[4] In fact, the specific-heat exponent α derived from $\nu_\perp$ of Eq. (1) is $\alpha=0.51$ for $N=\frac{4}{5}$, $\alpha=0.48$ for $N=\frac{5}{6}$, and $\alpha=0.44$ for $N=\frac{6}{7}$ which is not inconsistent with the predicted[21] value $\alpha=\frac{1}{3}$. Unfortunately, away from this multicritical point the $\nu_\perp$ values show a strong N dependence [also along the (2×1) phase boundary]; thus no reliable estimate for α is possible. Note that $\nu_\perp$ is determined from the slopes of $\xi_\perp(T, N^{-1})$ and usually shows stronger N dependence than T_c and $\nu_\perp/\nu_\parallel$ which are determined from the intersection of $Y_N(T)$.

The dashed line gives the disorder line $T_D(\theta)$ below which the wave vector φ is locked in at the (2×1) value $\varphi/2\pi=\frac{1}{2}$. Outside of this region φ_N varies continuously with T and θ. I could not find any scaling to the commensurate value $\varphi=\frac{2}{3}\pi$ which Ref. 4 predicts for parts of the "(3×1)" boundary.

The dotted line in Fig. 3 shows the exactly calculated temperature $T_6(\theta)$, where $\xi[T_6(\theta), N=6]=6$. While this line gives a good estimate of the (2×1) phase boundary, it fails to reproduce the "(3×1)" transition. This is due to the small value of $\nu_\perp/\nu_\parallel$ which means that $\xi_\perp$ grows with a small power of N only. For larger N values the dotted "(3×1)" region even shrinks somewhat since the correlated regions become more and more needlelike along the rows. Note that on a real surface one usually has only small homogeneous patches of less than 100 lattice spacings. Thus as a consequence of anisotropic scaling the experimental phase diagram might look more like the dotted line. In fact for H/Fe(110) a (3×1) phase is observed for $0.62<\theta<0.69$.[11]

As in any numerical calculation of finite systems one never can exclude the fact that there remain drastic effects which change the results qualitatively in the limit of infinite system size N. However, from experience with many other systems my results obtained from scaling to $N\to\infty$ indicate a new kind of a surface phase transition with anisotropic critical properties. The incommensurate critical wave vector and the be-

havior of the correlation length indicate an incommensurate ordered "(3× 1)" phase. Since such a phase should not exist according to present theories,[10] the nature of the "(3× 1)" phase is still unclear. Thus I hope that the present results will stimulate future experimental and theoretical work on uniaxial surface structures.

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