

Critical phenomena and defects in physisorbed layers

K Kern, IGV-KFA Jülich, Postfach 1913, 5170 Jülich, FRG

Structural phase transitions in two-dimensional systems are discussed with emphasis on transitions in which topological defects like domain walls, dislocations or steps have a key position. Experimentally, adsorbed monolayers on single crystal surfaces provide model systems for the realization of these phase transitions. We will discuss here some aspects of the structural phase transitions of Xe monolayers on Pt(111), Gr(0001) and Ag(111). The Xe-Pt(111) system exhibits a rich variety of 2D solid phases and corresponding mutual transitions, driven by the energetics and dynamics of domain walls in the Xe lattice. These domain wall defects are caused by the delicate interplay of the Xe-Xe and Xe-Pt interactions. Xe monolayers on Gr(0001) and Ag(111) have been discussed as model systems of dislocation induced melting, according to the Kosterlitz-Thouless-Halperin-Nelson-Young theory. We will show here that the corrugation of the substrate may indeed be responsible for the observation of a hexatic structure factor in the molten Xe monolayers, shedding some doubt on the intrinsic hexatic character of these liquid films. In addition to defects intrinsic to the adlayer, extrinsic defects due to the limited coherence of the substrate surface (finite step density) or due to small amounts of adsorbing impurities can substantially influence two-dimensional phases and their transitions. As an example we will discuss the impurity-quenched orientational epitaxy of Kr and Ar monolayers on Pt(111).

1. Introduction

In contrast to bulk (3D) phase transitions, phase transitions in two-dimensional systems (2D) are often high order transitions, with a continuous change of state from one phase to the other, in contrast to first order transitions, where a sudden rearrangement occurs. Continuous transitions are characterized by a critical behavior of a physical observable, which is the order parameter Ψ of the transition. Above the transition temperature T_c the thermodynamic average of the order parameter $\langle \Psi \rangle$ is zero, indicative of complete loss of long range order. Below T_c the value of $\langle \Psi \rangle$ is non-zero indicating long range order, and follows a power law when approaching the critical temperature: $\langle \Psi \rangle \sim (T_c - T)^\beta$. The order parameter can be the magnetization in ferromagnetic materials, the electron pair amplitude in superconducting materials, or the lattice distortion in crystals.

Continuous phase transitions are conveniently described in a phenomenological Landau free-energy expansion of the order parameter. In two-dimensional lattices two-component order parameters might be chosen, which are parameterized by an amplitude and a phase. While phase fluctuations dominate low-temperature behavior of 2D phases, amplitude fluctuations dominate at higher temperatures when approaching the critical temperature. Indeed, phase fluctuations, in form of long-wavelength phonons, are responsible for the suppression of a genuine long range order in two-dimensional solids, at all temperatures $T > 0$ K¹. Amplitude fluctuations, which are always present and dominate at the phase transition at high enough temperatures, appear in 2D systems in the form of defects, in particular as dislocations in 2D solids. Such dislocations (often termed domain walls or solitons) result by adding or removing a half-infinite row of atoms from an otherwise perfect lattice (Figure 1). They play a central role in phase transitions of quasi two-dimensional systems, in the melting transition as well as in the registry-disregistry transition².

The dominance of fluctuations in lower-dimensional systems can also be understood by simpler arguments. The order of a phase is thermodynamically determined by the free energy, i.e. by the competition between energy and entropy. In three-dimensional systems each atom has a large number of nearest neighbors (12 in a fcc crystal), thus the energy term stabilizes an ordered state, local fluctuations being of minor importance. In one dimension, however, each atom has only two nearest neighbors. Here the entropy term dominates the energy term, and even very small local fluctuations destroy the order. In a close packed two-dimensional system each atom has six nearest neighbors and, depending on temperature, energy and entropy may be in balance. As amplitude fluctuations, i.e. topological defects, can be excited thermally, the two-dimensional systems seem to be ideally suited for studying defect-mediated phase transitions.

Experimentally, adsorbed monolayers on single crystal surfaces provide model systems for the realization of 2D phases and their mutual transitions³. In analogy to bulk matter, these adsorbed layers can form quasi 2D gas, liquid or solid phases. Of particular interest are the solid phases; the substrate provides a periodic potential relief which interferes with the lattice structure of the monolayer, inducing modulations in the latter. In addition, the adatoms being of a different kind than the substrate atoms, the strength of the lateral interactions within the adlayer differs in general from the strength of the adsorbate-substrate interaction. Depending on the delicate balance between these forces and on structural relationships, the adsorbed monolayer can form ordered solid structures which are commensurate (in registry) or incommensurate (out of registry) with the substrate.

2. The commensurate-incommensurate (CI) transition in 2D

When the periodic modulation of the adsorption potential in the directions parallel to the substrate surface (e.g. the so called corrugation of the substrate surface) is dominant, the adsorbed

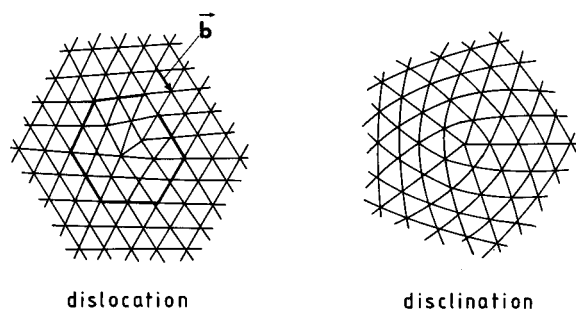


Figure 1. Dislocation and disclination of a triangular 2D-lattice. The Burgers vector, defined as the amount by which the path around the dislocation fails to close, is also shown.

adatoms only occupy the energetically most favored sites and form a structure commensurate with the underlying substrate. At the other extreme, when the adsorbate-adsorbate interaction dominates the periodic variation in the adsorbate-substrate interaction, the adlayer forms a structure which is determined by the dense packing of adatoms largely ignoring the substrate structure. This adlayer phase is termed incommensurate. Intermediate situations can, of course, occur in which only a certain fraction of the adatoms occupy preferred adsorption sites, and are termed high order commensurate. The existence of these HOC phases has only recently been demonstrated experimentally⁴. Only when the lateral adatom interaction and the substrate corrugation are comparable, an ordered commensurate (C) adlayer can undergo a transition into an incommensurate (I) phase as a function of coverage or temperature. Most intriguingly, this CI transition is driven by the formation of line defects, so called misfit dislocations as was demonstrated first by Frank and van der Merwe⁵. These authors studied a linear chain of atoms with a lattice constant a placed in a sinusoidal potential of amplitude V and periodicity b , representing the mutual interactions of the atoms in the chain by springs with spring constant K . The calculations reveal that for slightly different lattice parameters of chain and substrate, i.e. for a weakly incommensurate adlayer, the lowest energy state is obtained for a system which consists of large commensurate domains separated by regions of bad fit. The regions of poor lattice fit are dislocations with Burgers vectors parallel to the length of the chain.

In two-dimensional systems domain walls are lines. In a triangular lattice there are three equivalent directions. Therefore, domain walls can cross. Using Landau theory, Bak, Mukamel, Villain and Wentowska (BMWV)⁶ have shown that it is the wall crossing energy, Λ , which determines the symmetry of the weakly incommensurate phase and the nature of the phase transition. For attractive walls, $\Lambda > 0$, a hexagonal network of domain walls (HI) will be formed at the CI transition because the number of wall crossings has to be as large as possible. This C-HI transition should be first order. For repulsive walls, $\Lambda < 0$, the number of wall crossings has to be as small as possible, i.e. a striped network of parallel walls (SI) will be formed in the incommensurate region. The C-SI transition should be continuous. The striped phase is expected to be stable only close to the CI phase boundary. At large incommensurabilities the hexagonal symmetry should be recovered in a first order S-HI transition. In Figure 2 we summarize the possible domain wall structures. Superheavy and heavy walls are characteristic for those systems in which the incommensurate phase is packed more densely than

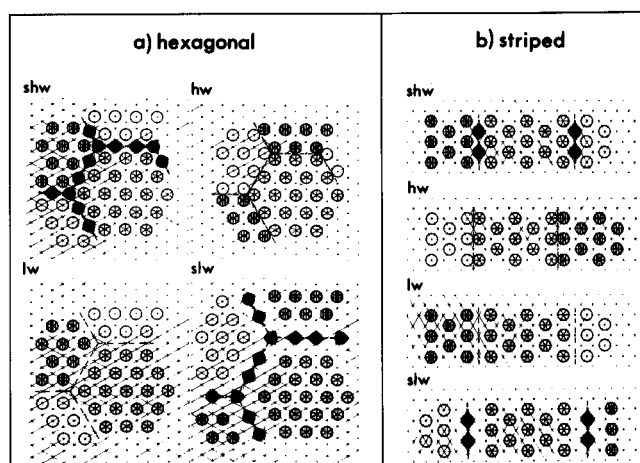


Figure 2. Domain wall systems for a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase on a triangular substrate lattice; (a) hexagonal and (b) striped symmetry. Abbreviations used: shw - superheavy, hw - heavy, lw - light, slw - superlight.

the commensurate phase while for light and superlight walls the opposite holds.

Perhaps the best known examples of the CI transition in 2D adlayer systems occur in the Kr monolayer on the basal (0001) plane of graphite⁷ and in the Xe monolayer on the Pt(111) surface³. Here we will discuss briefly the physics of the Xe-Pt system. In this adsorption system the Xe-Xe and Xe-Pt interactions favor Xe adsorption in the three-fold hollow sites of the Pt(111) surface. Below coverages of $\Theta_{Xe} \approx 0.33$ (Xe adatoms per Pt substrate atoms) and in the temperature range 60–99 K the xenon condenses in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ commensurate solid phase. This phase has very sharp diffraction peaks, characteristic for coherent Xe domains which are about 800 Å in size. As the Xe coverage is increased above 0.33, the relatively loosely packed Xe structure undergoes a transition from the commensurate $\sqrt{3}$ structure to an incommensurate striped solid phase with superheavy walls (see Figure 2)⁸. This weakly incommensurate solid is able to accommodate more Xe atoms than the commensurate phase by dividing into regions of commensurate domains separated by a regularly spaced array of striped denser domain walls. Increasing coverage causes the commensurate domains to shrink and brings the walls closer together. The domain walls are thus a direct consequence of the system's efforts to balance the competition between the lateral Xe-Xe and the Xe-Pt interactions. The C-SI transition can also be induced by decreasing the temperature below ~ 60 K at constant coverage ($\Theta_{Xe} \leq 0.33$); the driving force for this temperature induced CI-transition being anharmonic effects⁹.

The usual measure for the incommensurability of an I-phase is the misfit $m = (a_c - a_i/a_c)$, where a_c is the lattice parameter of the commensurate phase and a_i that of the incommensurate structure. For striped I-phases, the misfit has of course uniaxial character, being defined only along the direction perpendicular to the domain walls. Quantitative measurements of the misfit during the C-SI transition of Xe on Pt(111)⁸ have revealed a power law of the form,

$$m = \frac{1}{l} \propto (1 - T/T_c)^{0.51 \pm 0.04} \quad (1)$$

i.e. the distance between nearest neighbor walls l scales with the inverse square root of the reduced temperature. This square root dependence is the result of an entropy mediated repulsion between meandering nearest neighbor walls and is in accord with theoretical predictions¹⁰.

With increasing incommensurability the domain wall separation becomes progressively smaller until at a critical misfit of $\sim 6.5\%$ the Xe domain wall lattice spontaneously rearranges from the striped to the hexagonal symmetry (Figure 2) in a first order transition¹¹. A further increase of the incommensurability by adding more and more Xe eventually results in an adlayer rotation to misalign itself with the substrate in order to minimize the increasing strain energy due to the defect concentration. This continuous transition to a rotated phase (HIR) follows a power law $\phi \propto (m - 0.072)^{1/2}$ starting at a critical separation between nearest neighbor walls $l_c \simeq 10$ Xe-row distances¹¹.

At first glance, the existence of the various solid Xe phases on the hexagonal close packed Pt(111) surface seemed to be surprising. As already stated in the introduction, the various solid phases of adsorbed monolayers arise as a result of competing interactions; lateral adatom interaction vs the corrugation of the holding potential. In particular the commensurate $\sqrt{3}$ phase was unexpected; at 60 K the 'natural' two-dimensional Xe lattice parameter in the absence of any substrate would be about 8% smaller than the $\sqrt{3}$ distance on the Pt substrate (4.80 Å). In order to stabilize the commensurate Xe phase the corrugation of the substrate has to compensate this substantial strain and to counterbalance the attractive lateral Xe interaction, which has been measured to be $e_l^{\text{Xe-Xe/Pt}} = 43$ meV per atom¹².

It is indeed still a widespread belief that for rare gases adsorbed on close packed metal surfaces this corrugation is negligible. This belief originates in the very low corrugation of the interaction potential as deduced from He diffraction data. This argument, although found often in literature, is wrong and thus misleading. From small He corrugations it can not be inferred, that the lateral corrugation felt by all rare gases adsorbed on close packed metal surfaces is likewise small.

First, in diffraction experiments the He atoms probe the corrugation of the repulsive interaction potential in the region of positive energies, while adsorbed atoms feel the corrugation of the bottom of the attractive potential well, i.e. corrugations at two different locations on the potential curve. Second, and this is even more important, the interaction of the heavier rare gases Xe, Kr, Ar or even Ne differs appreciably from the interaction of He with the same substrate (e.g. the binding energy for He and Xe on Pt(111) are 4–6 meV and 277 meV respectively!).

In the framework of a simple Lennard-Jones type two body gas-surface potential the corrugation in the unit cell of a particular surface is entirely determined by the ratio σ/a , with σ being the Lennard-Jones diameter of the gas atom and a being the nearest neighbor distance in the substrate surface, and by the magnitude of the binding energy V_0 ¹³. In this model, the energy difference between adsorption of a Xe atom in a hollow and in a bridge position, $V_{\text{H-B}}$, amounts to $\sim 0.01 V_0$ for the (111) surfaces of Pt and Ag (both metals have similar atomic radii). Taking the actual binding energies for Xe adsorption on these surfaces^{14,15}, the Xe corrugation amounts to ~ 3 and ~ 2 meV, respectively.

The Lennard-Jones potential is only a crude approximation of the interaction between a rare gas atom and a metal surface. Drakova *et al*¹⁶ demonstrated recently in a self consistent Hartree-Fock calculation, that the corrugation of the rare gas-transition metal surface potential is substantially enhanced by

the hybridization between occupied rare gas orbitals and empty metal d orbitals. For the interaction of a Ne atom with the (110) surface of Cu, Ag and Pd, these authors calculated the corrugation of the short bridge site, $V_{\text{H-SB}}$, to increase from 0.04 V_0 (Cu) over 0.08 V_0 (Ag) to 0.27 V_0 (Pd). Based on the Pd(110) value we can estimate the bridge corrugation $V_{\text{H-B}}$ of the (111) surfaces of Pd and Pt to about 0.07–0.08 V_0 . This value is also consistent with the semiempirical Xe-Pd potential, recently developed by Girard and Girardet¹⁷ in order to explain the experimentally observed face specificity of the binding energy and of the induced dipole moment. For Pd(111) these authors evaluated $V_{\text{H-B}} \simeq 0.10 V_0$.

This large corrugation has been confirmed recently in experiments and in molecular dynamics studies of Xe adsorption on Pt(111). From the Xe coverage dependence of the isosteric heat of adsorption, Kern *et al*¹⁵ determined the corrugation of the Xe-Pt(111) potential to about 10% of the binding energy which is ~ 30 meV. A somewhat lower value of ~ 10 meV was needed by Black and Janzen¹⁸ in order to stabilize the commensurate $\sqrt{3}$ Xe phase in their molecular dynamics simulation. Note, that these values are compatible with values of diffusion barriers which represent roughly the corrugation. For instance, the diffusion barrier of Xe on W(110) (a rather close packed surface) has been measured to 47 meV¹⁹.

3. 2D melting and the 'hexatic' phase

One of the most fundamental phase transitions is the melting of a solid phase into a liquid. Theorists have predicted that in 2D systems melting may be a continuous process in which defects play a dominant role, quite in contrast to bulk matter where the melting transition is strictly first order and defects seem to be less important. The 2D melting theory discussed most frequently in the literature is the Halperin-Nelson-Young (HNY) model²⁰, which is based on the dislocation unbinding theory of Kosterlitz and Thouless²¹. From an experimentalist point of view the HNY theory basically applies to incommensurate solid monolayers which can be translated freely parallel to the substrate surface, so called 'free-floating solids'. According to HNY the melting transition from the 2D solid to the 2D liquid occurs via two continuous transitions. In the solid phase, only bound pairs of thermally generated dislocations are thermodynamically stable. At a temperature T_M , these dislocation pairs unbind. Since the isolated dislocations are quite effective in destroying translational order but less disruptive of orientational correlations (see Figure 1), an orientationally ordered but positionally disordered fluid phase is formed. This new phase is usually cited as 'hexatic phase' due to the conserved six-fold orientational order. Subsequently, this hexatic phase melts at a temperature T_i into an isotropic liquid. This second transition is driven by the decay of free dislocations into disclinations (Figure 1).

Although incommensurate physisorbed monolayers should be ideal realizations of systems with continuous melting, experimental results on these systems are contradictory and heavily disputed. The melting of submonolayers of Ne, Xe, CH₄ and O₂ on the basal plane of graphite seems to be first order, while Ar and C₂H₂ submonolayers on graphite as well as complete Xe monolayers on graphite and on Ag(111) seem to exhibit a continuous melting transition²².

The direct microscopic proof of the melting mechanism by analysing the orientational structure of the molten monolayers just above the transition has only recently been tackled. The

diffraction pattern of an isotropic liquid without orientational order is a ring. In the hexatic phase with partial conserved orientational order, however, the ring will split into six azimuthally broadened elliptical spots centered around the ultimate Bragg positions. In the HNY model the orientational order of the hexatic phase is due to the hexatic stiffness κ_A of the adsorbed monolayer, and the aspect ratio $(\kappa_\phi - \kappa)/\kappa$, which is the excess azimuthal width κ_ϕ to the polar width κ of the first order diffraction peak, is predicted to be constant independent of the temperature. For molten hexatic Xe monolayers an aspect ratio of $(\kappa_\phi - \kappa/\kappa) \simeq 4$ is predicted.

Detailed measurements of the structure factor of molten Xe monolayers have been reported recently by Nagler *et al*²³ on the basal plane of graphite, and by Greiser *et al*²⁴ on the close packed Ag(111) surface. In both studies the diffraction peak from Xe monolayers just above the melting point is found to have an azimuthal width 4 times the polar width, consistent with the predictions of the HNY model of the hexatic phase. However, we have to take into account that the corrugation of the substrate holding potential tends to align the orientation of the adlayers along specific substrate azimuths. The six-fold symmetry of the Gr(0001) and the Ag(111) surface generates a hexagonal orientation field having an effect comparable to the hexatic order parameter in the intrinsic hexatic phase. Nagler *et al*²³ have calculated the structure factor of an isotropic fluid monolayer in a strong hexagonal orienting field and found again a six-fold pattern of azimuthally broadened elliptical spots, whose aspect ratio is likewise found to be a constant scaling with the substrate corrugation. Taking the usually accepted values of ~ 3 meV for Xe-Gr(0001)¹³ and the above estimated value of ~ 2 meV for Xe-Ag(111) the aspect ratio for isotropic molten Xe films on these substrates is calculated to be about 4, in excellent agreement with the experimental observations.

The hexatic character of molten Xe films on Ag(111) and Gr(0001) seems to be predominately due to the orienting field of the substrate corrugation and not intrinsic to the 2D Xe liquid.

4. Extrinsic defects

Almost any theoretical study of adsorbed layers deals with perfect substrates, i.e. strictly periodic arrangements of surface atoms extending over infinite distances. In experiment, however, this situation is hardly met. Indeed, unavoidable slight misorientations of the substrate plane with respect to the low-index planes during crystal surface preparation result in a finite step density. Today's best prepared low-index metal surfaces have step densities of $\sim 0.1\%$, corresponding to average domain sizes of perfect coherence of ~ 2000 – 3000 Å. In addition, even under the most careful experimental uhv conditions (base pressure in the low 10^{-11} mbar range), small amounts of adsorbing impurities (H_2O , H_2 , CO) cannot be completely avoided. These extrinsic defects can have a dramatic influence on phase transitions of adsorbed layers²⁵.

We have demonstrated recently²⁶ that depending on the presence or absence of minute amounts ($\sim 0.1\%$) of preadsorbed impurities, Kr monolayers may be aligned ($R0^\circ$) or rotated by 30° ($R30^\circ$) with respect to the Pt(111) substrate, respectively. We have been able to demonstrate in a direct experiment that when

the Kr atoms are allowed to nucleate at the residual $\sim 0.1\%$ step sites of the substrate (the binding energy at step sites is $\sim 25\%$ larger than on terrace sites²⁷) the $R30^\circ$ orientation is obtained; on the contrary, when the step sites are blocked by preadsorbed CO or H the growing Kr layer has to nucleate on terraces and is aligned ($R0^\circ$) with the substrate.

This orientational pinning of adsorbed layers by substrate steps is not a matter of corrugation, at least as far as mobile adsorption is concerned (corrugation $\leq 10 k_B T$). Step pinning being a kinetic process and mobile adatoms are always bound first at non-blocked step sites due to the larger binding energy than on terrace sites, the orientation of an adsorbed layer can be decisively influenced by the kinetics of the layer growth with steps or defects as nucleation centers, even in the case of strongly corrugated substrates.

Acknowledgements

Stimulating discussions with George Comsa and Peter Zeppenfeld are gratefully acknowledged.

References

- H Wagner, *Z Phys*, **206**, 465 (1967).
- D R Nelson, In *Phase Transitions and Critical Phenomena* (Edited by C Domb and J L L Lebowitz), Vol 7, p1. Academic, New York (1983).
- K Kern and G Comsa, In *Chemistry and Physics of Solid Surfaces VII* (Edited by R Vanselow and R F Howe), p 64. Springer, Berlin (1988).
- K Kern, P Zeppenfeld, R David and G Comsa, *Phys Rev Lett*, **59**, 79 (1987).
- F C Frank and J H van der Merwe, *Proc R Soc*, **A198**, 216 (1949).
- P Bak, D Mukamel, J Villain and K Wentowska, *Phys Rev*, **B19**, 1610 (1979).
- E D Specht, A Mak, C Peters, M Sutton, R J Birgeneau, K L D'Amico, D E Moncton, S E Nagler and P M Horn, *Z Phys*, **B69**, 347 (1987); S C Fain, M D Chinn and R D Diehl, *Phys Rev*, **B21**, 4170 (1980).
- K Kern, R David, P Zeppenfeld, R L Palmer and G Comsa, *Solid St Commun*, **62**, 361 (1987).
- M B Gordon and J Villain, *J Phys*, **C18**, 3919 (1985).
- V L Pokrovsky and A L Talapov, *Soviet Phys JETP*, **51**, 134 (1980).
- K Kern, *Phys Rev*, **B35**, 8265 (1987).
- K Kern, P Zeppenfeld, R David and G Comsa, *J Vac Sci Technol*, **A6**, 639 (1988).
- W Steele, *Surface Sci*, **36**, 317 (1973).
- J Unguris, L W Bruch, M B Webb and J M Phillips, *Surface Sci*, **114**, 219 (1982).
- K Kern, R David, P Zeppenfeld and G Comsa, *J Electron Spectrosc Rel Phenom*, **44**, 215 (1987); *Surface Sci*, **195**, 353 (1988).
- D Drakova, G Doyen and F V Trentini, *Phys Rev*, **B32**, 6399 (1985).
- C Girard and C Girardet, *Phys Rev*, **B36**, 909 (1987).
- J Black and A Janzen, *Surface Sci*, **21**, 199 (1989).
- J R Chen and R Gomer, *Surface Sci*, **94**, 456 (1980).
- D R Nelson and B I Halperin, *Phys Rev*, **B19**, 2457 (1979); A P Young, *Phys Rev*, **B19**, 1855 (1979).
- J M Kosterlitz and D J Thouless, *J Phys*, **C6**, 1181 (1973).
- K J Strandburg, *Rev Mod Phys*, **60**, 161 (1988).
- S E Nagler, P M Horn, T F Rosenbaum, R J Birgeneau, M Sutton, S G J Mochrie, D E Moncton and R Clarke, *Phys Rev*, **B32**, 7373 (1986).
- N Greiser, G A Held, R Frahm, R L Greene, P M Horn and P M Suter, *Phys Rev Lett*, **59**, 1706 (1987).
- J Villain, *J Phys (Paris) Lett*, **43**, 1551 (1982); M Kardar and D R Nelson, *Phys Rev Lett*, **55**, 1157 (1985).
- K Kern, P Zeppenfeld, R David and G Comsa, *Phys Rev Lett*, **57**, 3187 (1986).
- R Miranda, S Daiser, K Wandelt and G Ertl, *Surface Sci*, **131**, 61 (1983).