THEORY OF ADSORBATE INDUCED
SURFACE RECONSTRUCTION ON
W(100)

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Abstract

We report results of a theoretical study on an adsorbate induced surface reconstruction. Hydrogen adsorption on a W(100) surface causes a switching transition in the symmetry of the displacements of the W atoms within the ordered c(2 × 2) phase. This transition is modeled by an effective Hamiltonian, where the hydrogen degrees of freedom are integrated out. Based on extensive Monte Carlo renormalisation group calculations we show that the switching transition is of second order at high temperatures and of first order at low temperatures. This behavior is qualitatively explained in terms of an XY model where there is an interplay between four and eight fold anisotropy fields. We also compare the calculated phase diagrams with a simple mean field theory.
1. Introduction

Structural phase transitions have been observed on a number of surfaces. One of the most extensively studied systems undergoing a surface reconstruction is the clean $W(100)$ surface (see e.g. [1,2,3] and references therein). It has a very rich phase diagram with a reconstructive phase transition from a $(1 \times 1)$ phase into a $c(2 \times 2)$ phase [1,4,5,6]. The microscopic structure of the low temperature phase was unraveled early by Debe and King [5] and it has since then been accepted that this phase involves alternate displacements of the $W$ atoms along the $<11>$ direction in the surface plane. A number of first principles total energy calculations [e.g. 7,8,9] have verified the inherent instability of the ideal $(1 \times 1)$ phase towards this reconstruction, and the Debe-King structure is found to have the lowest energy. There was some dispute on the nature of the high temperature phase, and thus also on the details of the structural phase transition between these two phases. Earlier, there was both experimental [1,10,11,12] and theoretical [13] evidence which was interpreted in favor of an ordered high temperature phase where the tungsten atoms would vibrate about their ideal bulk positions. The other possibility was that the tungsten atoms would be displaced from their bulk positions also in the high temperature phase but the displacements would point into random directions, thus forming a disordered phase [7,14]. Recent experimental [6,15,16] and theoretical [17,18,19,20] studies have corroborated the disordered nature of the high temperature phase, and it is now generally accepted that the transition is of order-disorder type instead of a displacive one.

While the clean surface of $W(100)$ has been studied extensively both experimentally and theoretically, the influence of adsorbates on the reconstruction has been studied to a far less extent and in most cases a thorough understanding of these phenomena is missing. Among the adsorbates, the adsorption of hydrogen has been
studied in most detail [1,4,10,22,23,26,27,44]. It was found that small amounts of hydrogen enhance the inherent instability of the clean surface, and increase the critical temperature of the order-disorder transition [21]. The structure with adsorbed hydrogen was initially believed to be the same as the clean surface reconstructed $c(2 \times 2)$ phase or very similar to it [1,5,22,23]. It was later shown [10] and verified [4,44] that the hydrogen adsorbed surface has a different structure when the coverage exceeds $\theta \simeq 0.1$. Namely, the clean $c(2 \times 2)$ has a $p2mg$ symmetry whereas the hydrogen rich (coverage $\theta > 0.1$) $c(2 \times 2) - H$ phase has a $c2mm$ symmetry. The symmetry change was cleverly verified by Griffiths et al. [24] in a low energy electron diffraction (LEED) spot intensity study. They studied the difference in the relative intensities of two half-order beams, namely $(\frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, \frac{1}{2})$ at a normal incidence. The difference between these two beams is finite in the reconstructed clean surface $p2mg$ phase, and it vanishes when the entire surface has switched into the $c2mm$ phase. This symmetry switching was *initiated* at a coverage of $\theta \simeq 0.04$ and completed at $\theta \simeq 0.16$. Similar symmetry switching has been observed in an infrared spectroscopy study [25]. The $c2mm$ phase is interpreted as due to a structure in which the $W$ atoms have alternate displacements along the $<10>$ or $<01>$ directions.

The hydrogen induced switching of the $W(100)$ surface between these two structures is the main subject of the present work. Our study is motivated by theoretical [26] and experimental [24] indications that the switching transition could be of first order at low temperatures, instead of being an $XY$ like continuous transition [27]. We will first briefly discuss the theoretical model for this work. For the clean surface, we adopt a lattice dynamical Hamiltonian which has recently been shown to describe the critical properties of the $W(100)$ surface very accurately [17,18,19,20]. It corresponds to an $XY$ model with an intrinsic cubic anisotropy field. To this model then, we add the short range interactions of hydrogen with its
nearest neighbor \( W \) atoms. The hydrogen degrees of freedom are then explicitly integrated out leaving an effective Hamiltonian. This new Hamiltonian is shown to contain anisotropy fields of all orders allowed by symmetry, and we argue that the nature of the switching transition at low temperatures is dictated by the interplay between effective fourth and eighth order anisotropy fields. We then proceed to calculate the details of the phase diagram, using first simple mean field arguments to locate the line of switching transitions on the \((T, \mu)\) - plane. To study the nature of the transition in detail, we present results of extensive Monte Carlo Renormalisation Group calculations. These results show that at high temperatures the transition is continuous, while below a multicritical point \( T_t \) it becomes discontinuous. Finally, we summarize our results and discuss the relevance of our work to experimental studies. Preliminary results have been previously reported [28].

2. Theoretical Models

As discussed above, it has been experimentally verified that hydrogen induces a \textit{switching} transition where the \( H \) atoms adsorbed on bridge sites pin the displaced \( W \) atoms towards themselves resulting in displacement orientations along either \(< 10 >\) or \(< 01 >\) direction, instead of the clean surface \(< 11 >\) direction. This reconstruction has been subject to theoretical investigations (\textit{e.g.} [3,8,9,26,27,29,30,31]) but to a far less extent than the clean \( W(100) \) surface.

The models discussed below, as well as our model belong to the class of so called lattice dynamical models which are written in terms of lattice displacements. When studying the driving forces for the transition, microscopic details have to be included in the model. However, lattice dynamical models are usually sufficient to study the critical properties of the systems under consideration. The role of
the detailed electronic degrees of freedom in these models has been discussed by various authors [3,32,33].

2.1 Lattice Dynamical Models

To study the effect of an adsorbate on the switching transition on the $W(100)$ surface, Lau and Ying [27] suggested a lattice dynamical model Hamiltonian

$$H = H^{\text{clean}} + H^{\text{ad}}. \quad (1)$$

In their work, the clean surface term $H^{\text{clean}}$ is of the type suggested by Fasolino et al. [34], with the details left unspecified. The crucial point is that for the clean $W(100)$ surface, it has the symmetry of an $XY$ model with cubic anisotropy. The intrinsic anisotropy of the clean surface is such that the $W$ atoms are displaced along the $<11>$ direction in the reconstructed $c(2 \times 2)$ phase. The adsorbate part $H^{\text{ad}}$ in Eq. (1) was chosen to be

$$H^{\text{ad}} = \frac{1}{2} \sum_{i',j'} J_{i',j'} n_{i'} n_{j'} + \sum_{i,i'} n_{i'} v(\vec{R}_i^0 + \vec{u}_i - \vec{R}_{i'}) \quad (2)$$

which describes the effects of hydrogen on the structural transition. In Eq. (2), $n_{i'}$ is an occupation number, and $J_{i',j'}$ is an interaction term between hydrogen atoms. The second summation describes the interaction between hydrogen and tungsten atoms as a sum of pair potentials $v$ where $\vec{R}_{i'}$ is the coordinate of a hydrogen adsorption site and $\vec{R}_i^0$'s denote the ideal bulk positions of the surface tungsten atoms. The addition of $\vec{u}_i$ describes the spontaneous displacements of the surface atoms.

Lau and Ying [27] started from Eq. (2) and found that the adsorbate induces a cubic anisotropy field that opposes the intrinsic clean surface one. This adsorbate
induced anisotropy will then increase in magnitude with coverage leading to the change of sign of the total anisotropy field. Hence the switching occurs from the phase in which \( W \) atoms are displaced along the \(<11\>\) directions to a phase in which they are displaced along the \(<10\>\) directions, favored by the opposing cubic term. This conclusion was supported by electronic band structure calculations [29] where it was suggested that even at low hydrogen coverages it would be energetically favorable for the surface atoms to align along the \(<10\>\) or \(<01\>\) directions in the low temperature \( c(2 \times 2) \) phase with hydrogen atoms on bridge sites. Fasolino et al. [35] suggested the switching to occur at a coverage of \( \theta \simeq 0.044 \simeq (\frac{2}{a\xi})^2 \) where \( a \) is the lattice constant and \( \xi \) is the surface coherence length. This value for switching agrees with LEED studies [24].

Ying and Roelofs [3,36] developed the model further by choosing for the clean surface Hamiltonian

\[
H^{\text{clean}} = \sum_i \left\{ \frac{A}{2} u_i^2 + \frac{B}{4} u_i^4 + 8 h_{i4}^0 u_{ix}^2 u_{iy}^2 \\
+ C_1 (u_{ix} u_{jx} + u_{ix} u_{kx} + u_{iy} u_{jy} + u_{iy} u_{ky}) \right\},
\]

where \( u_i \) is the displacement of the surface \( W \) atom at the \( i^{th} \) lattice site, and \( u_{ix} \) and \( u_{iy} \) are the \( x \) and \( y \) components of the displacement, respectively. \( A \) and \( B \) are coefficients of a simple double well potential, \( C_1 \) is the nearest neighbor interaction term, and \( h_{i4}^0 \) is the clean surface cubic anisotropy field. For the clean \( W(100) \) surface \( h_{i4}^0 < 0 \) which aligns the displaced \( W \) atoms along the \(<11\>\) directions. Summation \( i \) in Eq. (3) goes over all lattice sites.

Using (2) and (3), Ying and Roelofs obtained an effective \( H^{\text{eff}} \) to describe the hydrogen effects by integrating out the hydrogen degrees of freedom in the mean
field approximation, and working with a constant coverage description. However, this description breaks down if the transition happens to be of first order as we shall discuss below. Also, the approximation of retaining only the lowest order anisotropy fields is not justified for strong $H - W$ coupling as addressed below.

In a closely related computer study, Sugibayashi et al. [26] used an extended anisotropic $XY$ model to describe the clean surface, with a two-body lattice gas model for the adsorbate part. They presented results from their computer simulations for the switching transition, but were not able to conclude the nature of the transition at low temperatures. Their results seem to indicate, however, that there is a phase coexistence region at low temperatures between the $<11>$ and $<10>$ phases, which would be strong evidence for a first order transition.

2.2 New Model for H/W(100)

To be able to study a possible first order regime, and to give a more accurate description of the low temperature phase we have undertaken simulations of a new lattice dynamical model. The clean surface contribution in our model is that described by Eq. (3) to which we have added an additional eight fold anisotropy field:

$$H_{\text{clean}} = \sum_i \left\{ \frac{A}{2} u_i^2 + \frac{B}{4} u_i^4 + 8h_0^0 u_{ix}^2 u_{iy}^2 + C_1 (u_{ix} u_{jx} + u_{ix} u_{kx} + u_{iy} u_{jy} + u_{iy} u_{ky}) + h_8^0 \cos(8\phi_i) \right\},$$

(4)

where $\phi_i = \arctan(u_{iy}/u_{ix})$ is the displacement angle. To calculate the total surface - adsorbate partition function, we will make the simplifying assumption of neglecting direct $H - H$ interactions. Thus, we can write
\[ Z = \text{Tr} \{ n_{i' \nu}, \{ u_i \} \exp[-\beta (H^\text{clean} + H^\text{ad})] \} \] (5)

with \( H^\text{ad} = \sum_{i' \nu} n_{i' \nu} (V_{i' \nu} - \mu) \), where the summation \( i \) goes over all lattice sites and \( i' \) over all bridge sites. As usual \( \beta = 1/(k_B T) \), \( n_{i' \nu} \) is the actual hydrogen occupation number at a bridge site \( i' \), \( V_{i' \nu} \) is the interaction potential between hydrogen and surface tungsten atoms, \( \mu \) is the chemical potential, and \( u_i \) is the displacement vector of a tungsten atom. Next, we sum over all hydrogen degrees of freedom to obtain

\[ Z = \text{Tr} \{ u_i \} \exp[-\beta (H^\text{eff})], \] (6)

where \( H^\text{eff} \) is an effective Hamiltonian, which can be obtained in a straightforward fashion as

\[ H^\text{eff} = H^\text{clean} - k_B T \sum_{i' \nu} \log \{ 1 + \exp[-\beta (V_{i' \nu} - \mu)] \}. \] (7)

The summation \( i' \) goes over all bridge sites. They can also be labelled as \( i' \equiv (i, \nu) \) in which there are two bridge sites \( \nu \) associated with each lattice site \( i \). The interaction \( V_{i' \nu} \) is obtained by expanding a pairwise interaction potential to lowest order in the \( W \) atom displacements. This gives us \( V_{i,\nu} = \sum_j \alpha_{i j \nu} \cdot \vec{u}_j \) where the components of \( \alpha \) are given by \( \alpha_{i11} = (-\alpha, 0), \alpha_{i12} = (\alpha, 0), \alpha_{i21} = (0, -\alpha), \) and \( \alpha_{i22} = (0, \alpha) \), and \( \vec{u}_j = (u_{jx}, u_{jy})^T \), and \( \alpha \) is an effective interaction parameter between hydrogen and tungsten atoms. The relative positions of \( H \) and \( W \) atoms as well as displacement vectors are illustrated in Fig. 1.

The Hamiltonian (7) is written in terms of the chemical potential whereas the experiments are carried out at a constant coverage. The description of the
adsorbate in terms of the chemical potential rather than the coverage allows us to better investigate the possibility of both a first and a second order switching transitions. The coverage can be calculated and is given by the expression

\[ \theta = < \sum_{i, \nu} \frac{1}{\exp[\beta(V_{i, \nu} - \mu)] + 1} > \]  

in which the summation \( i, \nu \) goes over all bridge sites and the average \(< >\) denotes an average over configurations. Since there are two bridge sites for each \( W \), the maximum allowed coverage is normalized to the value of two.

### 2.3 Effect of the Anisotropy Fields in the Model for H/W(100)

We can predict qualitatively the behavior described by \( H^{\text{eff}} \) if we express it entirely in terms of the displacement angles \( \phi_i \) for fixed amplitudes instead of the displacement vectors \( \vec{u}_i \). If we retain only the isotropic nearest neighbor coupling terms and the leading anisotropy fields in the on-site potential we then obtain a simplified Hamiltonian

\[ H_{XY}^{\text{eff}} = K \sum_{i,j} \cos(\phi_i - \phi_j) - h_4(T, \mu) \sum_i \cos 4\phi_i + h_8(T, \mu) \sum_i \cos 8\phi_i. \]  

The anisotropy fields \( h_4(T, \mu) = h_4^a(T, \mu) + h_4^0 \) and \( h_8(T, \mu) = h_8^a(T, \mu) + h_8^0 \) where superscripts 0 and a refer to clean surface and adsorbate induced terms, respectively. This Hamiltonian is an XY model with both four and eight fold anisotropies.

The form of \( H^{\text{eff}} \) together with the dependence of \( h_4 \) and \( h_8 \) on \( T \) and \( \mu \) has important consequences for the expected behavior of the \( H/W(100) \) system since renormalisation group analysis [37] tells us that the four fold field is relevant at
all temperatures \( T < T_C \). For small values of \( \mu \), \( h_4(T, \mu) < 0 \) which favors the orientation of the \( W \) atoms along the \(<11>\) directions. However, since \( h_4^0(T, \mu) \) is a monotonically increasing function of \( \mu \) (for a fixed \( T \)), there will be a point \((\mu_{sw}, T_{sw})\) where \( h_4(\mu_{sw}, T_{sw}) = 0 \). Beyond this, \( h_4(T, \mu) > 0 \), and the minimum energy state is now given by \( W \) atoms displaced along the \(<10>\) directions. This simple analysis predicts that the switching transition in the \((T, \mu)\) - plane is determined by the condition \( h_4(\mu_{sw}, T_{sw}) = 0 \), and it is an \( XY \) transition of Kosterlitz - Thouless type [37,38,39]. Physically, for the clean surface, the intrinsic four fold field \( h_4^0 < 0 \) indicating a preference of the displacements for the \( W \) atoms along the \(<11>\) directions. As \( H \) is adsorbed, it sits on the bridge sites and the \( H - W \) interaction energy is minimized if locally the displacements of the nearest neighbor \( W \) atoms switch and point along the \(<10>\) or \(<01>\) directions. This local distortion has a finite range. Globally, the average \( h_4(T, \mu) \) is still negative for low hydrogen coverages. However, the effective \( h_4(T, \mu) \) now increases with the coverage or the chemical potential, reflecting these local distortions around each \( H \) atom.

To understand the nature of the switching transition in more detail, we must also consider the effect of the eight fold anisotropy field \( h_8(T, \mu) \) which is induced by the \( H - W \) interaction term in (7). It is well known that the eight fold field is relevant at low temperatures but above some \( T_t < T_C \) it becomes irrelevant [37]. When the eight fold field is negative, it favors orientations \( \phi = n \frac{\pi}{4} \), \( n = 0, ..., 7 \), while for \( h_8(T, \mu) > 0 \) the preferred orientations are \( \phi = \frac{\pi}{8} + n \frac{\pi}{4} \), \( n = 0, ..., 7 \). This is demonstrated in Fig. 2. Consider first a fixed, negative \( h_8 \). The eight fold field favors the same directions which are also favored by both positive and negative \( h_4(T, \mu) \). Thus, when \( h_4(T_{sw}, \mu_{sw}) \rightarrow 0 \) from the negative side a relevant \( h_8(T, \mu) \) field keeps the system at the orientation \( \phi = \frac{\pi}{4} \). However, as soon as the four fold field is positive and finite, it dictates again the orientation of the system which
suddenly switches from $\phi = \frac{\pi}{4}$ to $\phi = 0$. Thus, the transition is expected to be of first order at low temperatures when the eight fold field is relevant and negative. However, the situation is changed above $T_t$ where $h_8$ becomes irrelevant. Then, at $h_4(T_{sw}, \mu_{sw}) = 0$ the system is a pure $XY$ model. The phase boundary thus has a multicritical point $T_t$ where $T_t$ and $T_{sw}$ coincide for some $\mu$. This is precisely the behavior for our choice of $H^{\text{clean}}$ as in (4) with a zero intrinsic eight fold field. The reason is that the hydrogen adsorbate induced four fold and eight fold fields are of the same sign, and thus compatible with each other.

For the case of a positive $h_8(T, \mu)$ which competes with the four fold field, more complicated behavior can result below $T_t$. We expect then the phase boundary separating the $<11>$ and $<10>$ phases to open up into two Ising-like transitions with an intermediate phase in between [40,41]. This is a subject of a separate study.

It should also be noted here that this discussion of four and eight fold fields is strictly speaking only qualitative for $H/W(100)$. As we discuss in the Appendix, higher order fields are comparable in magnitude with $h_4$ and $h_8$ for a realistic $H – W$ coupling. Therefore, the following mean field and Monte Carlo Renormalisation Group analyses are based on the full effective Hamiltonian of Eq. (7). In addition, although the switching transition occurs at $h_4(T, \mu) = 0$, this four-fold field should be a renormalized effective field in which the short wavelength details have been averaged away. Thus, even if we are able to extract correctly the bare $h_4$ field in the Hamiltonian, it still would not allow us to locate the switching point exactly. This is one more reason why the numerical work is absolutely necessary. The discussion above, however, is valuable in that it nicely brings about the physical ideas behind the change in the order of the switching transition.
3. Mean Field Estimate and the Choice of Parameters for the Switching Transition

Before setting out to an extensive numerical study of our effective Hamiltonian, it is useful to study the mean field solution for the switching transition. The mean field approximation is exact at $T = 0$ and thus at least at low temperatures it should yield reasonable results. At higher temperatures, the temperature fluctuations affect the transition, making the switching occur at a lower coverage or chemical potential than the mean field theory predicts.

The energy difference between the two phases that we denote by $\phi = \frac{\pi}{4}$ and $\phi = 0$ ($N$ is the number of tungsten atoms), is:

$$\Delta E = \left[ H_{\text{eff}}(\phi = \frac{\pi}{4}) - H_{\text{eff}}(\phi = 0) \right],$$  \hspace{1cm} (10)

where

$$H_{\text{eff}}(\phi = \frac{\pi}{4}) = 2Nh^0_4 + Nh^0_8 - k_B T \sum_{\nu,i} \log\left[1 + \exp\left(-\beta (V_{\nu,i}(\phi = \frac{\pi}{4}) - \mu)\right)\right]$$
$$+ N\left(\frac{A}{2} + \frac{B}{4} - 2C_1\right),$$  \hspace{1cm} (11)

and

$$H_{\text{eff}}(\phi = 0) = Nh^0_8 - k_B T \sum_{\nu,i} \log\left[1 + \exp\left(-\beta (V_{\nu,i}(\phi = 0) - \mu)\right)\right]$$
$$+ N\left(\frac{A}{2} + \frac{B}{4} - 2C_1\right).$$  \hspace{1cm} (12)

This can be simplified by noting that there are only four different kinds of energy changes related to the bridge sites (total of $2N$) that can take place:
\[ \Delta E = 2Nh_4^0 \]
\[ - \frac{N}{2} k_B T \log \left[ \frac{1 + \exp(\beta(\sqrt{2} \alpha - \mu))}{1 + \exp(\beta \mu)} \right] \]
\[ - \frac{N}{2} k_B T \log \left[ \frac{1 + \exp(\beta(\sqrt{2} \alpha - \mu))}{1 + \exp(\beta(2 \alpha - \mu))} \right] \]
\[ - \frac{N}{2} k_B T \log \left[ \frac{1 + \exp(\beta(\sqrt{2} \alpha - \mu))}{1 + \exp(\beta(-2 \alpha - \mu))} \right] \]
\[ - \frac{N}{2} k_B T \log \left[ \frac{1 + \exp(\beta(2 \alpha - \mu))}{1 + \exp(\beta(-2 \alpha - \mu))} \right] \]  

In order to study in more detail the low temperature behavior of the system, we set \( \Delta E = 0 \) and seek solutions to it. These solutions become exact at \( T = 0 \) in the absence of fluctuations.

At \( T = 0 \), we get \( \Delta E/N = \frac{1}{2} \mu_{sw} + 2h_4^0 + \alpha = 0 \) in the interval \(-2\alpha < \mu_{sw} < -\sqrt{2}\alpha\).

The solution for \( \mu_{sw} \) is then \( \mu_{sw} = 2(-2h_4^0 - \alpha) \) where \( \mu_{sw} \) is the value for the chemical potential where the switching between \(<11>\) and \(<10>\) phases occurs.

Thus, by fixing the values of \( \alpha \) and \( h_4^0 \) we can compare the prediction of the mean field theory with the experimentally observed values of coverage for the transition.

From the results we can also deduce a constraint between the four fold anisotropy field \( h_4^0 \) and the interaction parameter \( \alpha \) as \( 4|h_4^0| < (2 - \sqrt{2})\alpha \) which restricts the choice of parameters, as will be discussed below.

In our model, there is also a solution for a higher chemical potential which corresponds to the unphysical situation of switching back to the \(<11>\) phase at a higher coverage. This is due to our omission of direct interactions between hydrogen adatoms on adjacent bridge sites. A direct repulsion between the adatoms on these sites would eliminate this unphysical transition. Experimentally, many complicated structures \([4,25]\) have been observed at high hydrogen coverages and these are outside the present scope of study.

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We have worked with two different sets of parameters. The first set (set I) is very close to that of Yoshimori and coworkers [26] and was chosen so that direct comparison could be made with their results. We are particularly interested in answering the question whether the transition is of first order at low temperatures. Their results indicates this possibility but the conclusions were unclear. A notable point in this set of parameters is that the clean surface four fold field $h_4^0$ is very weak compared to other similar studies [17,18,19,20] or total energy calculations [8,9].

The other set of parameters (set II) is more consistent with experimental work and total energy calculations. A Hamiltonian based on this set of parameters has been successfully used to explain many clean surface phenomena [17,18,19]. However, to prevent a switching into displacements along directions other than $<10>$, we need to set the eight fold field $h_8^0$ of Eq. 4 to a negative value.

In what follows, we work with dimensionless displacements $\tilde{u}$ and temperature $\tilde{T}$ defined as $u = u_s \tilde{u}, T = T_s \tilde{T}$ where $T_s$ and $u_s$ are the scale factors. The numerical values for the first set of parameters are $\tilde{A} = Au_s^2/T_s = -2, \tilde{B} = Bu_s^4/T_s = 8.8, \tilde{C}_1 = C_1 u_s^2/T_s = 1.5, \tilde{h}_4^0 = -0.1, \tilde{\alpha} = 4.5, \text{ and } \tilde{h}_8^0 = 0$. The numerical values for set II are $\tilde{A} = Au_s^2/T_s = -10, \tilde{B} = Bu_s^4/T_s = 40, \tilde{C}_1 = C_1 u_s^2/T_s = 3.75, \tilde{h}_4^0 = -1.85, \tilde{\alpha} = 17, \text{ and } \tilde{h}_8^0 = -0.6$. The displacement amplitude $\tilde{u} = \sqrt{(4C_1 - A)/(B + 8h_4)} \simeq 1$ for parameter set I and is set to the value 1 for the second set. The critical temperature for the clean surface ($\mu = -\infty$) is about $\tilde{T}_C \simeq 1.3$ for the first parameter set and about $\tilde{T}_C \simeq 2.3$ for the other set. The experimentally observed values for $T_C \simeq 230K$ and $u \simeq 0.2 A$ yield the scale factors $u_s \simeq 0.2 \text{ and } T_s \simeq 175$ for the first set and $T_s \simeq 100$ for the second set. For simplicity, from here on throughout the paper we will always use the scaled values for the parameters, e.g. $T$ for $\tilde{T}$. 
The choice of $\alpha = 4.5$ in the first set of parameters follows of Roelofs and Ying [3]. In their approach, the effective Hamiltonian was obtained by keeping terms only to fourth order in the displacements of the $W$ atoms. The various parameters including $\alpha$ were then determined by comparing theoretical results with the experimental data. As we show in the Appendix, the higher order terms are quantitatively important and cannot be neglected. Indeed, the estimate for the clean surface anisotropy $h_0^0$ in ref. [3] is about an order of magnitude smaller than the current first principles results. Thus, the value of $\alpha = 4.5$ can also no longer be viewed a reliable estimate. In the second set of parameters, the anisotropy field is much stronger and close to the first principles result. As a consequence, the constraint $(2 - \sqrt{2})\alpha > 4|h_0^0|$ implies that a much larger value of $\alpha$ is required. Our choice of $\alpha = 17$ yields a switching coverage in agreement with the experimental observation. It is also consistent with the infrared vibrational spectroscopy data when the new larger value of the anisotropy field is taken into account.

Finally, we should note that a smaller value of $|h_0^0|$ makes the transition more XY-like and thus more difficult to analyze numerically whereas a larger value would decrease the fluctuations and result in more Ising like behavior in the vicinity of the transition with smaller finite size effects. Larger absolute values of the four fold field $h_4^0$ also hold the system preferrably in the $<11>$ direction and thus would move the switching to occur at a higher chemical potential. However, the parameters within the model cannot be changed arbitrarily as discussed above, and the value of $h_4^0$ imposes restriction to the value of the interaction parameter $\alpha$. Increasing $h_4^0$ means increasing $\alpha$, and this leads the switching to occur approximately at a constant coverage over a large temperature range. The qualitative behavior of these two parameter sets is the same both in the $(T, \mu)$ and in $(T, \theta)$ planes (latter not sketched here).
4. Numerical Results

To study the nature of the switching transition for the full Hamiltonian of Eq. (7), we have carried out extensive Monte Carlo renormalization group (MCRG) simulations [42]. By studying the cumulants of the order parameter, we have been able to determine the order of the transition both at low and high temperatures. These results are supported by our additional studies of the order parameter, its distribution function, coverage, and the observation of strong hysteresis at low temperatures, as we will elucidate below.

In the simulations, we have used the standard Metropolis updating scheme. They were carried out using a nonconserved order parameter and Glauber dynamics. The amplitudes of the tungsten atom displacements \( u_i \) were held fixed as it has been shown recently [17,18] that displacement amplitude fluctuations are not important for the critical behavior of this system. We studied mainly two system sizes, namely 64 \( \times \) 64 and 32 \( \times \) 32. Computational time involved with larger systems becomes rather formidable. The averages were computed over 50 000 configurations for parameter set I, and over 20 000 for set II.

In the MCRG studies, the lattice is divided into blocks of size \( L \), and we then study the cumulants of the moments of the order parameter distribution function. For this, we used two order parameters, namely

\[
< \Phi_x > = \frac{1}{L^2} \sum_i (-1)^{(i_x + i_y)} u_{xi} 
\]

\[
< \Phi_y > = \frac{1}{L^2} \sum_i (-1)^{(i_x + i_y)} u_{yi},
\]

where \( u_{xi} \) and \( u_{yi} \) are the \( x \) and \( y \) components of the displacement vector at the \( i^{th} \) lattice site, and \( i_x \) and \( i_y \) are the \( x \) and \( y \) coordinates of the \( i^{th} \) lattice site in
a block of size $L$. The coefficient $(-1)^{i_x+i_y}$ is a phase factor. $<>$ denotes an average over configurations, and the summation goes over all lattice sites. In the $<11>$ phase both (14) and (15) have finite values whereas in the transition to $<10>$ ($<01>$) phase $<u_x>$ ($<u_y>$) vanishes. There is no preference for one phase over the other. By studying the behavior of the cumulants of these average displacement components, we can probe the order of the switching transition.

The block cumulants used are defined by

$$U_{Li} = 1 - \frac{<\Phi_i^4>_L}{3 <\Phi_i^2>_L^2},$$

$$V_{Li} = 1 - \frac{<\Phi_i^4>_L}{2 <\Phi_i^2>_L^2} + \frac{<\Phi_i^6>_L}{30 <\Phi_i^2>_L^3},$$

where $i$ refers to $x$ and $y$. The variation of these two cumulants as a function of the block size $L$ depicts a flow diagram analogous to that of a renormalisation group method. It can be shown [42] that these cumulants approach zero above $T_C$ as the block size increases. Below $T_C$, both these cumulants tend to nonzero values $U_L \Rightarrow U^* = \frac{2}{3}$, $V_L \Rightarrow V^* = \frac{8}{15}$, and at a second order transition they tend to nontrivial values.

We also monitored the combined order parameter of Eqs. (14) and (15):

$$<\Phi> = \frac{1}{L^2} \sum_i (-1)^{i_x+i_y} u_{xi} u_{yi},$$

For the ordered $<11>$ phase this order parameter has a finite value, and in the $<10>$ phase it vanishes.

If the transition is of first order, one of the block cumulants is expected to flow towards the ordered state value of $\frac{2}{3}$ at all chemical potentials. As the
transition occurs suddenly between two ordered phases, one of the order parameter components does not vanish at the transition \( < u_y > \) for the \(< 01 \rangle \) phase and \( < u_x > \) for the \(< 10 \rangle \) phase) but abruptly changes from one ordered state value to the other. The other component vanishes suddenly at the transition \( < u_x > \) for the \(< 01 \rangle \) phase and \( < u_y > \) for the \(< 10 \rangle \) phase).

One should note that if the transition is very weakly of first order, it is very difficult to distinguish between it and a second order transition. This is true in our case in the vicinity of the multicritical point where the order of the transition changes.

In the following, we will present numerical data only for one parameter set (set I, Figs. 3 and 4) but will show the phase diagram for both parameter sets in Fig. 5. The reason for this is that results for both sets are qualitatively very similar, and the quantitative differences can be seen in the respective phase diagrams. For parameter set I, the switching occurs at approximately \( \theta \approx 0.02 \) which is lower than the experimentally observed value. For set II, we reproduce the switching at approximately \( \theta \approx 0.1 \) which is in good agreement with experiments [24].

4.1. High Temperature MCRG Results

Fig. 3 (a) shows the behavior for parameter set I at high temperatures \( (T = 1.4) \), and confirms our predictions for the second order transition. The switching transition in this case is from the \(< 11 \rangle \) state into the \(< 01 \rangle \) state, i.e. \( < u_x > \) vanishes. The cumulants \( U_{Lx} \) of \( u_x \) show behavior typical for a second order transition: in the \(< 11 \rangle \) phase \( (\mu < -12) \) the cumulants approach the fixed point of \( U_{Lx} \approx 0.67 \) and in the \(< 01 \rangle \) phase \( (\mu > 11.5) \) the cumulants approach zero. We estimate the transition to happen in the region where chemical potential is \(-12 < \mu < -11\). Inside this range of chemical potential, the cumulants approach a nontrivial fixed point \( (\mu \approx -11.5) \). The problematic behavior of the cumulants
at $\mu = -14$ is attributed to large fluctuations at this temperature and the vicinity of two phase transitions (order - disorder transition and switching).

When studying the cumulants of $< u_y >$, we see that in the ordered phase they approach the value of $U_{Ly} \approx 0.67$, and then near the transition they flow to a nontrivial fixed point at $\mu \in [-12, -11.5]$. At larger values of $\mu$ the cumulants again approach the ordered state value. The errors have been taken from the results from the largest lattice sizes.

Based on these results, we conclude that the switching transition at $T_{sw} = 1.4$ occurs at $\mu_{sw} \in [-12, -11.5]$, and it is of second order. Data for the parameter set II are very similar, and result in a switching transition for $T = 2.4 (< T_C$, high temperature) at $\mu_{sw} \in [-28.4, -28.0]$.

4.2 Low Temperature MCRG Results

In Fig. 3 (b) we depict the behavior of the cumulants at $T_{sw} = 0.5$ again for the parameter set I. At chemical potential values $\mu < -8.8$, the cumulants of $U_{Lx}$ all approach the ordered phase value. At $\mu > -8.8$, the cumulants vanish. The cumulant behavior of $U_{Ly}$ shows no change in behavior when passing through the transition but the cumulants approach the ordered state value of 0.67 at all chemical potentials. We interpret this as evidence of a first order phase transition into the $< 10 >$ phase at this temperature. The strange behavior of $U_{Ly}$ at $\mu = -8.8$ is probably to be due to strong metastable effects combined with slow dynamics of the system at these low temperatures.

Based on similar arguments, the switching for set II occurs for $T = 0.6$ at $\mu_{sw} \in [-26.7, -26.4]$. In this case the metastability effects seem to be less severe, and the accuracy of simulations is thus better even at relatively low temperatures.
4.3 Results from Other Quantities

Further qualitative support for the MCRG results can be found in our coverage studies. In Fig. 4 the coverage as in Eq. (8) is plotted as a function of temperature for different values of the chemical potential. If the transition were of first order a discontinuity in the real coverage would be observed at the transition. However, as we work with a finite system, we observe only a very sharp rise in coverage at the transition.

In the case of a second order transition, we would expect the coverage to increase gradually when the transition region is passed. The data in Fig. 4 is in qualitative agreement with the prediction of a first order transition at low temperatures and a second order transition a higher temperatures. The abrupt increase in coverage is very pronounced at $T = 0.2$. Similar behavior was also observed for the order parameter. The jump in coverage was very clear in simulations with set II parameters in the first order regime, and more gradual at higher temperatures reconfirming the qualitative similarity in simulations for both parameter sets.

In addition, we have observed strong hysteresis and phase coexistence (as determined from the order parameter distribution function) at low temperatures to further support the scenario for a first order transition. Hysteresis studies have not been performed for the second parameter set.

4.4 The Phase Diagram

Based on the mean field theory and our numerical results, we sketch phase diagrams for both parameter sets in Figs. 5 (a) and 5 (b) for the line of switching transitions as induced by hydrogen adsorption on the $W(100)$ surface. The temperatures for the $(1 \times 1) \rightarrow c(2 \times 2)$ transition both for the clean surface ($\mu = -\infty$) and for the low hydrogen coverages have been determined from MCRG studies. The solid order - disorder line is only a guide to the eye.
In both Figs. 5 (a) and 5 (b), the dashed line denotes the mean field solution. The solid line is the part of the switching transition where it is expected to be of second order, and the dotted line depicts the first order switching transition. The agreement with the mean field line is very good at low temperatures where the role of fluctuations is not important. At higher temperatures the deviations are due to temperature fluctuations which cause the system to undergo a phase transition at lower chemical potentials than our mean field results would imply. The mean field result for the parameter set II at higher temperatures deviates particularly strongly from the MCRG data.

The whereabouts of the multicritical point $T_t$ where the transition changes its order could not be accurately pinpointed by our simulations. The locations of the multicritical points depicted in Fig. 5 are only schematic. We expect it to be somewhere between $0.5 < T_t < 1.0$ for set I, and $1.0 < T_t < 1.5$ for set II. The error bars shown depict the variance of numerical results from a series of simulation runs.

5. Summary and Discussion

To summarize, we have developed a model Hamiltonian to describe the adsorbate induced effects on the $W(100)$ surface. The clean surface part consists of a lattice dynamical Hamiltonian, which describes the $(1 \times 1) \rightarrow c(2 \times 2)$ transition as studied by Han and Ying [17,18]. To include the hydrogen induced effects, we have considered a simple model of interactions between $W$ and $H$ atoms, and integrated out the hydrogen degrees of freedom to obtain an effective Hamiltonian. This leads to an $XY$ model with anisotropy fields of all orders allowed by symmetry. In particular, the interplay between the fourth and eighth order anisotropy fields indicates that the switching transition should be first order at low temperatures and of second order at high temperatures. This prediction was confirmed by Monte
Carlo renormalisation group calculations, and further corroborated by studies of other quantities. We also used the MCRG studies together with a simple mean field theory to map out the line of switching transitions on the \((T, \mu)\) plane.

We have carried out simulations with two rather different sets of parameters, and obtained qualitatively similar behavior for both sets. With set I, we have been able to reproduce results similar to those of Sugibayashi et al., and re-interpret their findings in terms of first and second order transitions. The transition coverage is somewhat lower than experimentally observed. The second parameter set is more in agreement with total energy calculations, and the results are qualitatively same as for the first set. These both parameter sets reveal qualitatively similar behavior. Thus, regardless of the strength of the four fold anisotropy field in an experimental sample, a change in the order of the switching transition should be observed as a function of temperature.

Experimental evidence from an infrared spectroscopy (IR) study supports the scenario for a second order transition at room temperature. In their study, Arrecis et al. [25] observe only one peak in their IR spectra over the coverage range \(\theta \in [0.044, 0.22]\). If there were coexisting phases present, this would show as additional peaks in the spectra corresponding to the different symmetries of the phases. The LEED study of Griffiths et al. was performed at lower temperatures \((T \simeq 200 \, K)\) although the temperature was not held constant [24]. Their data shows indications of a coexistence region between \(\theta \in [0.05, 0.16]\) which could be interpreted in favor of a first order transition. The temperature range in Ref. 24 is somewhat higher than our predictions but is in qualitative agreement with our work. Very recently, Okwamoto [43] has presented results of mean field calculations on the model of Lau and Ying [27] showing the switching transition to be of first order at all temperatures below the order - disorder line. However, it should be
noted that as the cubic anisotropy field vanishes at the transition, Okwamoto’s method is equivalent to treating the pure XY model with a mean field theory. In this case it is well known that the mean field treatment does not predict the order of the transition correctly as the angular spin fluctuations destroy conventional long range order.

The major drawbacks in this study were the slow dynamics of the model and the finite size effects. These together made it impossible for us within given computer time to locate the multicritical point more accurately. In addition, the adsorbate induced part generates all allowed anisotropy fields which complicates the analysis. From an experimental point of view, however, the location of the multicritical point may vary from sample to sample, depending on the possible intrinsic eight fold field. Thus a more accurate theoretical determination of $T_c$ may not prove to be necessary after all.

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Appendix

In this Appendix, we will discuss the hydrogen induced anisotropy fields in more detail. We shall first write a series expansion for the part of the Hamiltonian which is due to the adsorbate. We shall then expand the $H - W$ interaction potential in terms of the anisotropy fields, and discuss the convergence of this expansion.

We start from the adsorbate induced part of Eq. (7) and denote fugacity by $\gamma = \exp(\beta \mu)$. The summation $i$ goes over all lattice sites and $\nu$ over both bridge sites on each lattice site. Notation is in all cases equivalent to that in the text.

\[
H_{\text{eff}} - H_{\text{clean}} = -k_B T \sum_{i,\nu} \log(1 + e^{-\beta (V_{i,\nu} - \mu)}) \tag{A.1}
\]

\[
= -k_B T \sum_{i,\nu} \left[ \gamma \exp(-\beta V_{i,\nu}) - \frac{\gamma^2}{2} \exp(-2 \beta V_{i,\nu}) \pm ... \right] \tag{A.2}
\]

\[
= -k_B T \sum_{i,\nu} \left[ \gamma \sum_n (-\beta)^n \frac{(V_{i,\nu})^n}{n!} - \frac{\gamma^2}{2} \sum_n (-2 \beta)^n \frac{(V_{i,\nu})^n}{n!} \pm ... \right] \tag{A.3}
\]

\[
= -\sum_{i,\nu,n} (-\beta)^{n-1} \frac{(V_{i,\nu})^n}{n!} \left[ \gamma - \frac{2^n \gamma^2}{2} + \frac{3^n \gamma^3}{3} \pm ... \right] \tag{A.4}
\]

\[
= -\sum_{i,\nu,n} (-\beta)^{n-1} \frac{(V_{i,\nu})^n}{n!} \sum_{k=1}^{\infty} \gamma^k (-1)^{(k+1)} k^{(n-1)} \tag{A.5}
\]

\[
def = -\sum_{i,\nu,n} (-\beta)^{n-1} \frac{(V_{i,\nu})^n}{n!} F_n(\gamma, \mu) \tag{A.6}
\]

Next, we study the effect of the $H - W$ interaction terms $\sum_{i,\nu} (V_{i,\nu})^n$ which generate all the anisotropy fields induced by the hydrogen degrees of freedom. Due to symmetry arguments, the odd powers of $\vec{u}$ vanish. Let us now for the sake of argument consider the term in Eq (A.5) for $n = 4$: 
\[ \sum_{i,\nu}(V_{i,\nu})^4 = \sum_{i,\nu} \left[ \sum_j (\alpha_{i\nu j} \cdot \vec{u}_j) \sum_k (\alpha_{i\nu k} \cdot \vec{u}_k) \right. \]
\[ \left. \sum_m (\alpha_{i\nu m} \cdot \vec{u}_m) \sum_n (\alpha_{i\nu n} \cdot \vec{u}_n) \right] \], \quad (A.7) \]

which reduces to

\[ \sum_{i,\nu}(V_{i,\nu})^4 = \sum_{i,\nu,j} [\alpha_{i\nu j} \cdot \vec{u}_j]^4 \] \quad (A.8)

when we consider only the on-site terms.

On the other hand, based on symmetry arguments we can readily write the expansion for (A.1) in a general form when we consider contributions only from the on-site terms:

\[ H_{\text{eff}} - H_{\text{clean}} = \sum_i \sum_{k=0}^{\infty} h_{4k}^a(T, \mu) \cos(4k\phi_i) \] \quad (A.9)

where \( \phi_i \) is the displacement angle. The terms where \( k = 1 \) and 2 correspond to the analysis in Sec. 2.3.

When we now expand Eq. (A.8) in terms of the displacement angle \( \phi \), and note that \( \vec{u} = (u_x, u_y)^T, |\vec{u}| = u_0, u_x = u_0 \cos \phi, u_y = u_0 \sin \phi \) and \( |\alpha_{i\nu j}| = \alpha \), we get a contribution for the four fold anisotropy field as

\[ -\frac{k_B T}{4!} \left( \frac{\alpha u_0}{k_B T} \right)^4 \left[ \gamma - 8\gamma^2 + 27\gamma^3 - 64\gamma^4 + \ldots \right] \] \quad (A.10)

However, it is important to notice that this is not the total adsorbate induced field \( h_{4}^a(T, \mu) \). Namely, the evaluation of higher powers of \((V_{i,\nu})^n\) in Eq. (A.5) results in contributions not only to \( h_{4}^a \), but also to lower order anisotropy fields.
These contributions can be of the same order of magnitude as the leading terms which severely hampers the analysis of these expansions. Thus, for example, for the coefficient of the four fold anisotropy field we obtain

\[
h_4^a(T, \mu) = -\frac{k_B T}{4!} \left( \frac{\alpha u_0}{k_B T} \right)^4 F_4(\mu, T) - \frac{3k_B T}{6!} \left( \frac{\alpha u_0}{k_B T} \right)^6 F_6(\mu, T)
- \frac{7k_B T}{8!} \left( \frac{\alpha u_0}{k_B T} \right)^8 F_8(\mu, T) - \frac{15k_B T}{10!} \left( \frac{\alpha u_0}{k_B T} \right)^{10} F_{10}(\mu, T)
- \frac{495k_B T}{12!} \left( \frac{\alpha u_0}{k_B T} \right)^{12} F_{12}(\mu, T) \pm ... \tag{A.11}
\]

where \( F_n(\mu, T) \) is defined by \((A.5)\) and \((A.6)\).

To study analytically the interplay between the cubic and eighth order anisotropy fields, and the vanishing of the total \( h_4(T, \mu) \) at the switching transition, one must first ensure the overall convergence condition \( \exp\{-\beta (V_{i,\nu} - \mu)\} \leq 1 \). Unfortunately, for the values we have used for the parameters \( \alpha, \mu \) and \( T \), this condition is not usually met in the vicinity of the switching transition line. We have also verified this numerically. In addition, for the parameters that we use, the term \( \alpha u_0/(k_B T) \) is never less than one for physically reasonable temperatures, thus further hampering the convergence of \((A.11)\). The additional effect of the more complicated off-site terms, which involve products of cosines at different lattice sites, is also difficult to determine accurately but it seems evident that they should be included in a quantitatively accurate calculation.
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Figure captions

Figure 1

Here we show schematically the relative positions of $W$ and $H$ atoms on the $W(100)$ surface. The solid dots (●) denote the ideal $W$ atom positions, and the vectors $\vec{u}_i$ denote the positions of the displaced $W$ atoms. The hydrogen atoms reside on the bridge sites ($\times$) $i' = (i, \nu)$ where $i$ denotes the tungsten atom lattice sites, and $\nu = 1, 2$ the two bridge sites related to each lattice site. The $H$ atoms feel the $W$ atom potential of the nearest sites only, e.g. $V_{ii} = -\alpha u_{ix} + \alpha u_{kx}$, cf. Eq. (7). We have also depicted the magnitudes of the displacements and the lattice constant.

Figure 2

(a). The eight directions favored by the positive and negative four fold anisotropy fields. The dotted directions are favored by a negative $h_4$ and the solid lines show directions favorable for a positive $h_4$. A negative eight fold field $h_8$ favors all these directions. (b). The eight directions favored by a positive eight fold field. Compared to (a) these directions are rotated by $\frac{\pi}{8}$.

Figure 3

(a). MCRG cumulant behavior typical for a second order transition at $T = 1.4$, and (b) for a first order behavior at low temperatures ($T = 0.5$) for parameter set I. See text for details.

Figure 4

Coverage (Eq. (8)) increases as a function of the chemical potential. At elevated temperatures the increment takes place smoothly whereas at lower temperatures an abrupt increase is seen. The latter would indicate a possible first order
transition at low temperatures as discussed in the text. The calculation is performed for parameter set I.

**Figure 5**

The phase diagrams for $H/W(100)$ in the $(T, \mu)$ plane, based on numerical simulations of our model Hamiltonian for parameter sets I (a) and II (b) The solid dots denote the MCRG results. The switching transition changes order at $T_t$ above which the transition is of second order (solid line), and below which it is assumed to be of first order (dashed line). The dotted line shows the mean field result. The solid line between the ordered and disordered phases in (a) is only a guide to the eye.