Effect of H Adsorption on the Displacive Transition of W(001) Surface

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A theoretical model is proposed for understanding the effect of H adsorption on the displacive transition of the W(001) surface. The coupling of the H adatoms to the substrate distortion leads to an enhancement of the displacive transition and a change in the overall symmetry. This is consistent with the features observed in low-energy electron diffraction for the H/W(001) chemisorption system.

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Hydrogen adsorbed on W(001) is one of the most studied chemisorption systems.[1] In the low-energy electron diffraction (LEED) study of H/W(001),[2] it has been well established that a $c(2\times 2)$ pattern is formed at low coverages followed by a splitting of the half-order spots at higher coverages. However, many puzzling questions remain in the interpretation of the data. One basic difficulty is to reconcile the $c(2\times 2)$ order at low coverages with the strength of the lateral interaction among H adatoms.[3] In addition, the weak scattering power of H atoms cannot account quantitatively for the intensity of the half-integral–order spots.[4] Recently, displacive phase transition has been observed on the clean W(001) surface[5-7] with a LEED pattern very similar to that of H-covered surfaces. This suggests immediately that a theoretical understanding of the H/W(001) chemisorption system has to include the possibility of a substrate distortion as well as lateral interaction among the adatoms. In this paper, we propose a theoretical model which shows that the adatom-substrate interaction leads to an enhancement of the displacive transition and a change in the overall symmetry.[8] These are precisely the features observed in LEED at low coverages.[9-11]

At or above room temperature, the mobility of the adatoms is sufficiently high for them to reach thermal equilibrium. The Hamiltonian describing the adatoms in the presence of a substrate distortion can be written as

$$H_{\mathrm{ad}} = \tfrac{1}{2}\sum_{i',j'} J_{i'j'} n_{i'} n_{j'} + \sum_{i,i'} n_{i'} v(\vec{R}_i{}^0 + \vec{u}_i - \vec{R}_{i'}). \tag{1}$$

Here $\vec{R}_{i'}$ is the coordinate of the possible binding site for H and $n_{i'}$ is the occupation number. The sites are chosen to be the twofold-symmetric bridge sites as indicated by vibrational-spectroscopy data,[12] and $J_{i'j'}$ is the H-H interaction with strengths J_1 and J_2 between nearest and next-nearest neighbors (Fig. 1). The second term in (1) describes the H-W interaction as a sum of pair potentials v. This differs from the conventional lattice-gas model in that the possibility of a substrate atom displacement from the periodic position $\vec{R}_i{}^0$ to $\vec{R}_i{}^0 + \vec{u}_i$ is included in the Hamiltonian. In this paper, we shall examine how this coupling of the adatom to the substrate-atom displacement affects the displacive transition of the W surface.

LEED studies[4,9] indicate that in the distorted phase of W, the surface-atom displacement is modulated with wave vector $\vec{K} = (\pi/a)(1,1)$ where a is the lattice constant, and that the direction of the displacement is parallel to the surface.[13] The distortion vector can therefore be described by two order parameters φ_1 and φ_2, which are the amplitudes of the frozen-in M_5 phonons, as follows:

$$\vec{u}_i = a(\varphi_1 \hat{K}\cos\vec{K}\cdot\vec{R}_i{}^0 + \varphi_2 \hat{K}'\cos\vec{K}'\cdot\vec{R}_i{}^0), \tag{2}$$

where $\vec{K}' = (\pi/a)(1,-1)$ and $\hat{K}$ and $\hat{K}'$ are unit vectors along $\vec{K}$ and $\vec{K}'$, respectively. In the presence of a periodic lattice distortion described by (2), the binding energy of H over the bridge sites is also modulated periodically with the same wave vector. Hence the average occupation number $\bar{n}_{i'}$ takes the form

$$\bar{n}_{i'} = \tfrac{1}{2}\theta + n'\cos\vec{G}\cdot\vec{R}_{i'} + m_1\sin\vec{K}\cdot\vec{R}_{i'} + m_2\sin\vec{K}'\cdot\vec{R}_{i'}. \tag{3}$$

Here θ is the coverage with $\theta = 1$ defined as one H atom per surface W atom. In addition to modulations of wave vector $\vec{K}$ and $\vec{K}'$ in response to the substrate distortion, a modulation of $\vec{G} = \vec{K} - \vec{K}'$ is also allowed by symmetry. This has the effect of allowing the average occupation number on A and B sites (Fig. 1) to be different from each other.

In the mean-field approximation, the free energy corresponding to H_{ad} in (1) can be easily obtained as[14]

$$F_{\mathrm{ad}} = -N[2\lambda(m_1\varphi_1 + m_2\varphi_2) + 4(J_1 - J_2)n'^2 + 4J_2(m_1^2 + m_2^2)] + T\sum_{i'}[\bar{n}_{i'}\ln\bar{n}_{i'} + (1-\bar{n}_{i'})\ln(1-\bar{n}_{i'})], \qquad (4)$$

where N is the number of W surface atoms, T is the temperature, $\bar{n}_{i'}$ is given by (3) and

$$\lambda = (i/a)\hat{K}\cdot\int d^2r\, e^{-i\vec{K}\cdot\vec{r}}\nabla v(\vec{r}). \qquad (5)$$

Equation (4) is the analog of a two-dimensional antiferromagnetic system with two interpenetrating lattices (A and B sites in Fig. 1). In the magnetic language, φ_1 and φ_2 are the staggered fields, and m_1 and m_2 are the staggered magnetizations. The mean magnetizations at the A and B sites are $\frac{1}{2}\theta \pm n'$. The chemical potential corresponds to a uniform external field. In arriving at (4), it has been eliminated in favor of the average coverage θ,[3] which is the independent variable in LEED experiments.

The amplitudes φ_1 and φ_2 describing the W-atom displacement are themselves thermodynamical variables. Recent electronic-structure calculations suggest that the driving mechanism for the displacive transition is either a Fermi-surface instability leading to a charge-density wave[15,16] or an intrinsic atomic instability with wave vector determined by the Fermi-surface structure.[17] Regardless of the detailed microscopic picture, the part of the free energy that depends on φ_1 and φ_2 can be described by a phenomenological Landau-Ginzburg expansion. The most general form allowed by the symmetry of the (001) face corresponding to M_5 distortion given in (2) is[18]

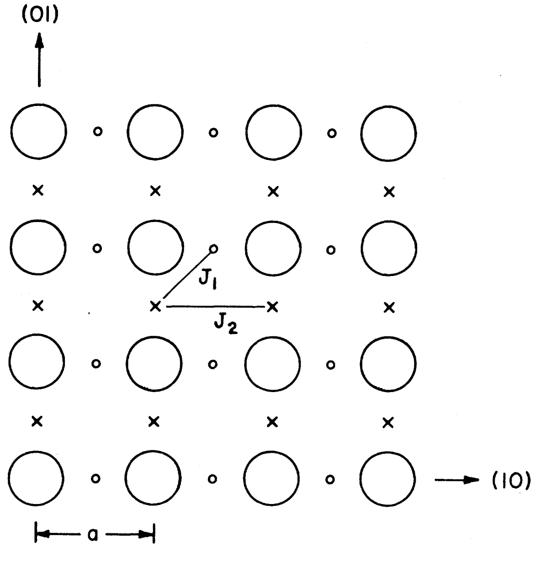

FIG. 1. Model of the unreconstructed substrate surface. The W atoms are denoted by large circles and the adsorption sites by small circles (A sites) and crosses (B sites). The nearest- and next-nearest-neighbor interaction constants are denoted by J_1 and J_2.

$$F_s = N[r(\varphi_1^2 + \varphi_2^2) + u(\varphi_1^2 + \varphi_2^2)^2 + v\varphi_1^2\varphi_2^2]. \qquad (6)$$

In addition to the direct H-W atom interaction as described by the second term in (1), the adsorbed H can also influence the surface electronic structure and lead to a possible coverage dependence of the coefficients r, u, and v. In the absence of detailed microscopic calculation of the surface electronic structure as a function of H coverage, as well as the knowledge of the precise driving mechanism, we shall regard these coefficients as coverage independent and concentrate on studying the consequences of the direct H-W coupling. It is also worth pointing out that the amplitude of distortion discussed here refers to a long-range order such as observed in LEED. It is not necessarily the relevant quantity for interpreting ion-scattering[19] or electron-energy-loss experiments,[12] in which even short-range order can play a significant role.

The total free energy is the sum of the contributions from (4) and (6): $F = F_{\mathrm{ad}} + F_s$. If we minimize F with respect to m_1, m_2, and n', express the result in terms of φ_1 and φ_2, and expand to quartic order, we obtain an expression of the same form as (6). The term proportional to $\varphi_1^2\varphi_2^2$ has coefficient $v' = v - \lambda^4\theta/6T^3$ to lowest order in θ. This is the so-called cubic anisotropy term which destroys the rotational invariance within the surface plane. For (i) $v' > 0$, minimization of F requires either $\varphi_1 = 0$ or $\varphi_2 = 0$, while for (ii) $v' < 0$, we have $\varphi_1 = \pm\varphi_2$. Case (i) corresponds to a distortion vector $\vec{u}$ in the (1,1) or (1,−1) direction and (ii) corresponds to $\vec{u}$ along (1,0) or (0,1). From the LEED data for the clean W surface, Debe and King[9] concluded that the surface-atom displacement is either along (1,1) or (1,−1). This implies $v > 0$. Since v' decreases with θ, at some finite value of the coverage, it will change sign and the displacement will switch to the (1,0) or (0,1) direction. This is consistent with LEED data for the H/W(001) surface.[9,11]

The quadratic term in the expansion of F has coefficient $r - \lambda^2/\alpha$, with $\alpha = 4T/(2\theta - \theta^2) - 4J_2$.

The additional term of $-\lambda^2/\alpha$ represents a lowering in energy for the distorted phase through the feedback effect of the H-W interaction. Consequently, the transition temperature, which is determined by the condition that $r-\lambda^2/\alpha$ vanishes, increases as a function of θ. Since r has the form $A(T-T_s)$ near the clean-surface transition temperature T_s, the transition temperature $T^*(\theta)$, to lowest order in θ, is

$$T^*(\theta)=T_s+\lambda^2\theta/2AT_s. \tag{7}$$

Minimizing the total free energy with respect to the order parameters, we obtain the following result for $v'>0$: $\varphi_2=m_2=n'=0$, and $\varphi_1=\varphi$ and $m_1=m$ are given by the solution of the coupled equations

$$\begin{aligned}&A(T-T_s)\varphi+2u\varphi^3-\lambda m=0,\\&-4J_2m+\frac{T}{2}\ln\frac{(\theta+2m)(2-\theta+2m)}{(\theta-2m)(2-\theta-2m)}-\lambda\varphi=0.\end{aligned} \tag{8}$$

It follows from the structure of (8) that the solutions $\varphi(\theta,T)$ and $m(\theta,T)$ satisfy the conditions $\partial|\varphi|/\partial\theta>0$, $\partial|m|/\partial\theta>0$ for $\theta<1$. Thus the amplitude of distortion φ increases monotonically with coverage at low coverage. This is again the consequence of the feedback effect of the H-W interaction. The result for the case $v'<0$ is similar. We note that the enhancement of the distortion amplitude is independent of the sign of the coupling constant λ. Referring to (1), (4), and (5), we see that for $\lambda>0$, the H-W binding energy is lower on bridge sites between pairs of W atoms that are closer together, while for $\lambda<0$, the binding energy is lower between pairs that are farther apart. In either case, the H will preferentially occupy adsorption sites with lower binding energy, resulting in a lowering of total energy.

To get a better quantitative feeling, we plot in Fig. 2 both the experimental[11] and theoretical curves for the half-integral-order spot intensity I as a function of temperature at different coverages. For the coherent scattering portion, I is proportional to φ^2, neglecting the weak scattering power of H.[4] At sufficiently low coverage, $v'>0$ so that the W displacement is along (1,1) or (1,−1), with φ given by the solution to (8). The value of T_s is deduced from the clean-surface I-vs-T curve at 276 K[11] and J_2 from desorption experiments[10,20] at 380 K. The value of u has been estimated to be 2.0×10^6 K from lattice-dynamic calculations,[21] and A is obtained from the amplitude of distortion, estimated to be 0.25 Å at low temperature from LEED intensity calculations.[4]

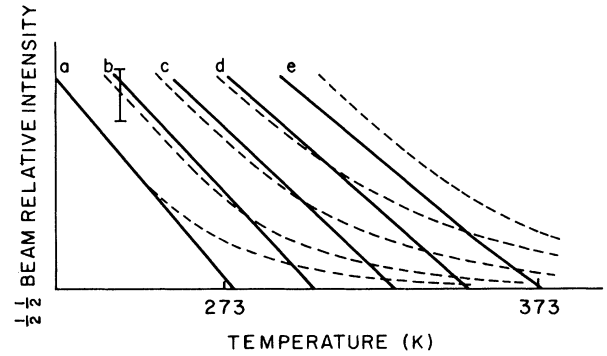

FIG. 2. Plots of $(\frac{1}{2},\frac{1}{2})$-beam intensity as a function of temperature at coverages (a) 0, (b) 0.036, (c) 0.072, (d) 0.107, and (e) 0.143. The dashed lines are experimental data (Ref. 11) and the solid lines are calculated values.

The only unknown parameter is the coupling constant λ, which is chosen to have the value 8000 K to give the best fit. As can be seen from Fig. 2, there is good agreement between theory and experiment for $t=|T-T^*|/T^*\gtrsim0.05$. Inside the critical region, φ deviates from the mean-field behavior of $t^{1/2}$. In addition, critical scattering becomes important, i.e., the intensity $I\propto\langle\varphi^2\rangle$ differs appreciably from $\langle\varphi\rangle^2$ as calculated from (8). Thus agreement is not expected for temperature close to T^*.

In summary, we have studied the effect of H-W coupling on the displacive transition on W(001) surface and found the following consequences: (i) The transition temperature and the distortion amplitude at a fixed temperature both increase monotonically with coverage, and (ii) the distortion vector switches direction from (1,1) to (1,0) at some coverage. These theoretical findings are in agreement with LEED results.[9-11] They follow from the general form of the linear coupling of the order parameters and do not depend on the precise values of the parameters in our model, such as the nearest- and next-nearest-neighbor interactions J_1 and J_2. Finally, we like to point out that at sufficiently low temperatures, the adatoms are no longer mobile, but act rather as quenched impurities. This could account for the observation that H adsorption at low temperatures destroys the displacive transition rather than enhancing it.[10,11]

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Self-Diffusion via Sine-Gordon Solitons

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Theoretical evidence is presented that for temperatures so low that k_BT is much less than the rest energy of a soliton, the mean square displacement of a diffusing particle of an infinite sine-Gordon chain behaves as $t^{1/2}$ for times much longer than microscopic times but much shorter than the soliton lifetime τ. For times much greater than τ, *linear* behavior is suggested. Finite-size effects are discussed in the context of recent computer simulation studies.

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The problem of the dynamical behavior of interacting particles subject to interactions with a heat bath which can be simulated by random forces of the Langevin type has applicability to a wide variety of systems in physics, chemistry, and biology.[1] One such nontrivial system with essential nonlinearities is the sine-Gordon chain, which consists of a chain of particles, each moving in a sinusoidal potential and interacting with each other via nearest-neighbor spring forces. We will deal with the simplest case, where the natural length of the spring is equal to the period of the sinusoidal potential. Though there exist particular solutions to the dynamical equations of motion of the system in the absence of random forces,[2] we still do not have an exact solution for