cling, with gyrofrequency, bounce frequency, and drift frequencies more disparate than the normal frequencies in the RECE-Berta device, resonances of sizable width would exist only very close to field reversal.

We thank D. E. Baldwin, W. C. Condit, H. H. Fleischmann, T. K. Fowler, S. C. Luckhardt, L. D. Pearlstein, and G. R. Smith for helpful discussions. This work was performed under the auspices of the U. S. Department of Energy at Lawrence Livermore Laboratory under Contract No. W-7405-ENG-48.

[1]S. C. Luckhardt and H. H. Fleischmann, Phys. Rev. Lett. 39, 747 (1977).
[2]B. V. Chirikov, "A Universal Instability of Many-Dimensional Oscillator Systems" (to be published).
[3]D. V. Anderson, to be published.
[4]D. D. Ryutov and G. V. Stupakov, Dokl. Akad. Nauk. SSSR 240 (1978) [Sov. Phys. Doklady (to be published)].
[5]R. H. Cohen, to be published.

Hydrogen on Tungsten(100): Adsorbate-Induced Surface Reconstruction

R. A. Barker and P. J. Estrup
Department of Physics and Department of Chemistry, Brown University, Providence, Rhode Island 02912

Chemisorbed hydrogen on a tungsten(100) surface produces major effects in two regions of the adatom density, at $\rho_1 \simeq 3 \times 10^{14}$ and $\rho_2 \approx 5 \times 10^{14}$ H atoms/cm^2. Changes at ρ_2 are probably caused by conventional adatom-adatom interactions, but the effects at ρ_1 appear to have a different origin and we propose that hydrogen produces displacement waves in the metal surface which gradually disappear above ρ_1. This type of adsorbate-induced reconstruction may also have been observed for H on Mo(100) and Cs on W(100).

Although hydrogen adsorbed on the (100) face of tungsten is one of the best known examples of chemisorption, recent reviews[1,2] of this system conclude that none of the existing models provides a consistent description of the experimental facts. A basic difficulty is that the overlayer structure deduced from low-energy electron-diffraction (LEED) patterns[3,4] does not correlate with several other surface properties, including the adatom density.[5] To explain the inconsistencies we propose that in addition to conventional interactions between neighboring adatoms a different phenomenon occurs: a modification of the surface electronic structure whereby *hydrogen adsorption induces a surface reconstruction* similar to the one seen at low temperature on clean W(100).[4,6-8] A simple relationship between the coverage and the surface structure is not expected in this case.

Previous discussions have ascribed the observed effects to the occupation of sites on an undisturbed substrate. The surface has 10×10^{14} W atoms/cm^2 and must provide about twice this number of sites for hydrogen since the adsorption is dissociative at all coverages[9] and since the saturation coverage is about 17×10^{14} H atoms/cm^2.[5,10] According to thermal desorption spectra (TDS)[11] and theoretical calculations,[12] the dom-

inating lateral interaction is a repulsion between adatoms on adjacent sites. The surface properties should therefore vary smoothly with ρ, the adatom density, until nearest-neighbor (nn) pairs no longer can be avoided, i.e., when $\rho \approx 5 \times 10^{14}$ cm^{-2} and at this density, referred to as ρ_2, a drop in the desorption energy is expected.[13] Furthermore, the repulsions should give rise to a $c(2\times2)$H structure having its maximum degree of long-range order when $\rho = \rho_2$. Only some of these predictions are confirmed by experiment.

Figure 1 shows the work function change, $\Delta\varphi$, upon exposure. Previous point-by-point measurements[3,5] resulted in an almost structureless curve, but when $\Delta\varphi$ is monitored continuously[14] an inflection at $\Delta\varphi \approx 0.16$ eV is seen (Fig. 1, left). A second feature (not shown) is a knee at $\Delta\varphi \approx 0.27$ eV which is present only at elevated temperatures. If the saturation density is 17×10^{14} cm^{-2}, these features occur at $\rho_1 \sim 3 \times 10^{14}$ and $\rho_2 \approx 5 \times 10^{14}$ cm^{-2}, respectively. The latter correlates with the pronounced drop in the desorption activation energy E_d seen on the right in Fig. 1. The shape of the E_d curve agrees with the nn-interaction model[11,13] and it accounts for the two peaks in the TDS and the knee in the $\Delta\varphi$ curve at ρ_2. However, it does not explain the inflection at ρ_1.
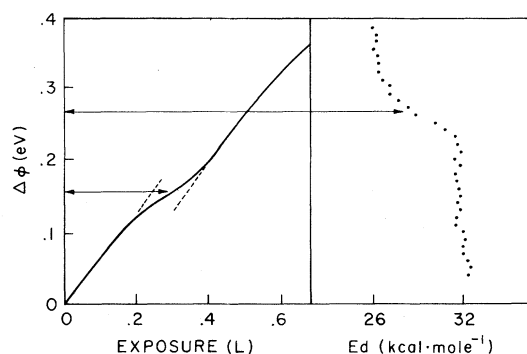
FIG. 1. Plots of $\Delta\varphi$, the work-function change, and E_d, the activation energy for desorption. On the left is shown $\Delta\varphi$ at room temperature as a function of hydrogen exposure (1 L = 10^{-6} Torr sec); its value at saturation is 0.9 eV. The feature at 0.16 eV could be present in either $\Delta\varphi(\rho)$ or the sticking probability $s(\rho)$; to rule out the latter would require independent measurements of s. At the coverage corresponding to $\Delta\varphi = 0.27$ eV, E_d drops, as shown on the right. E_d was obtained from a family of isobars; the method (Ref. 14) provides relative values of E_d and the absolute energy scale has been chosen to agree with results from thermal desportion spectra (Ref. 2 and 11).
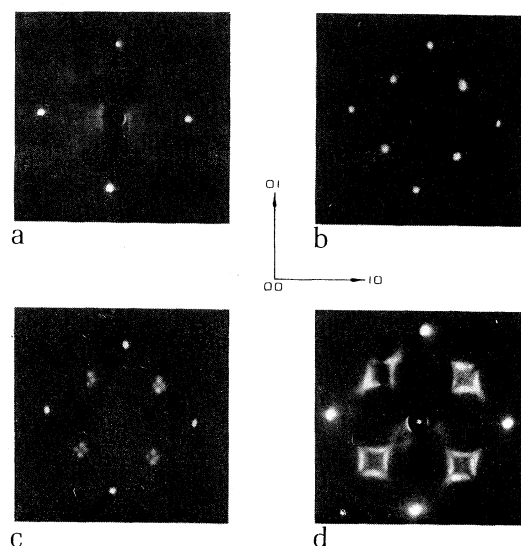

FIG. 2. LEED patterns produced by adsorption of hydrogen on W(100) at room temperature. The primary beam energy is 48 eV. (a) Clean W(100); hydrogen-atom density (b) $\rho \approx 2.5 \times 10^{14}$ cm^{-2}, (c) $\rho \approx 3.7 \times 10^{14}$ cm^{-2}, and (d) $\rho \approx 7 \times 10^{14}$ cm^{-2}.

LEED patterns for W(100)/H are shown in Fig. 2. At room temperature, $\frac{1}{2}\frac{1}{2}$ spots [Fig. 2(b)] are formed which subsequently split [Fig. 2(c)] and rapidly weaken, later producing the streaky and curved diffraction features seen in Fig. 2(d). It has been assumed that the nn interactions first give rise to a $c(2\times2)$H structure and then cause the formation of antiphase domains[3,15] thereby producing the observed patterns. However, this interpretation offers no rationale for the curved diffraction features in Fig. 2(d) and it fails to explain why the splitting occurs at a density well below ρ_2.[14,16] We have found that the splitting coincides with the step in $\Delta\varphi$, i.e., occurs at ρ_1.

Major changes at either ρ_1 or ρ_2 are also observed in other experiments. ESD (electron stimulated desorption)[5,17,18] gives a maximum H$^+$ yield at ρ_1; in ELS (electron energy loss spectroscopy)[19] a new loss peak appears at ρ_2; UPS (ultraviolet photoelectron spectroscopy)[20] shows rapid shifts in the spectrum near ρ_1; and the curves obtained by SRS (surface reflection spectroscopy)[21] change slope at ρ_1. There is some uncertainty in these coverage assignments; however, in the present work the E_d, $\Delta\varphi$, LEED, and ESD measurements were made on the same sample, in the same chamber, and in some cases at the same time, so that relative coverages should be reliable. As mentioned, the change at

ρ_2 in E_d may be explained by nn interactions and a weakening of the bond at this density is evident also in ELS. On the other hand, changes at ρ_1 show up mainly in experiments designed to probe the surface electronic structure. The new periodicities seen by LEED therefore correlate with changes in the electronic structure and a comparison with LEED results for clean W(100) suggests that a surface reconstruction is involved.

We recently reported evidence for a temperature-induced phase transition on clean W(100) and Mo(100).[6] The reconstructed (low-temperature) phase on W(100) is characterized by a periodic lattice distortion (PLD) in the $\langle 11 \rangle$ direction with wavelength $a\sqrt{2}$ (a = lattice parameter) so that a $c(2\times2)$ structure is formed. When LEED $I(V)$ curves for the $c(2\times2)$ (clean) and $c(2\times2)$H surfaces are compared[8] only slight differences are found (although the latter has been reported[22] to have the higher symmetry) and the two structures are therefore believed to be very similar. Calculations indicate[8] that—contrary to previous assumptions—scattering from the H atoms contributes little to the LEED intensity and that in both structures the W-atom displacements are 0.15–0.3 Å. This agrees with recent ion scattering data[23] which show that top-layer W atoms are displaced $\gtrsim 0.2$ Å in the $c(2\times2)$H structure and that at 300 K displacements of W atoms occur

even in the absence of hydrogen—consistent with the diffuse $\frac{1}{2}\frac{1}{2}$ spots observed under these conditions.[6,23] Evidently the wavelength of the PLD depends on ρ; it is $a\sqrt{2}$ initially but changes rapidly at $\rho > \rho_1$ while the amplitude decreases, resulting in the splitting and weakening of the $\frac{1}{2}\frac{1}{2}$ spots. It is interesting that the wavelength also depends on the temperature; we find[14] that the $\frac{1}{2}\frac{1}{2}$ splitting [Fig. 2(c)] can be enhanced by increasing either ρ or T.

These structural changes presumably arise from vibrational and electronic instabilities of the surface[24-28] but a determination of the relevant energy terms is difficult. For clean W(100) and Mo(100) parts of the 2D band structure are known from angle-resolved UPS[29] and from calculations,[30,31] and recent studies show that the electronic energy is lowered by reconstruction.[32,33] A suggested mechanism[34] is the formation of a PLD coupled to a charge-density wave (CDW), similar to the phase transformations occuring in layered transition-metal chalcogenides[35,36] and the surface periodicity should then depend on the properties of the electrons near the Fermi level. W(100) has a peak in the surface density of states (SDOS)[30] just below E_F at $k_x = k_y \approx 0.5\pi/a$ which may be responsible for the $c(2\times2)$ geometry. In the case of the hydrogen-induced changes, this would be consistent with the observation that the $c(2\times2)$ structure and the peak in the SDOS disappear at the same coverage. It may also account for the $\frac{1}{2}\frac{1}{2}$ spot splitting [Fig. 2(c)] since calculations[31] indicate that the adsorbate gradually raises the surface bands relative to E_F and a change in the wavelength of the PLD is therefore expected. The curved streaks seen in the LEED patterns at higher coverages [Fig. 2(d)] may be an effect similar to the Fermi surface "imaging" obtained for $1T$-TaS_2[36] (ascribed to "phasons"[35]) and for alloys.[37]

The conclusion that the major LEED changes are due to substrate-atom displacements removes the conflict between the LEED patterns and the coverage measurements but it also implies that it will be difficult to determine the position of the H atoms by this technique. However, recent ELS data[38] show that H is in a "bridged" site, i.e., is bound to two W atoms, at all coverages. The distance between the two W atoms is reduced by the PLD[8,22] but returns to the value $a = 3.16$ Å as the lattice relaxes at high ρ; the accompanying changes in the W-H-W bonding are also detected by ELS.[38] Because of H-H interactions the adlayer must have at least some short-

range order at low ρ and will tend to a $c(2\times2)$ arrangement near ρ_2. In the region $\rho_1 < \rho < \rho_2$ the overlayer appears to be homogeneous rather than in islands. The evidence for this comes from co-adsorption experiments[14] in which the sample is exposed first to hydrogen until ρ_1 is reached and then to oxygen; the latter adsorbate immediately compresses the H layer, causing the $\frac{1}{2}\frac{1}{2}$ spots to split and develop as if additional hydrogen were being adsorbed. There is no evidence to rule out islands of hydrogen in the region $0 < \rho < \rho_1$ but if they exist they must have a focal density $< \rho_1$.

On a cold sample (~ 150 K), H adsorption does not produce the sequence of Fig. 2, nor does it give an inflection in $\Delta\varphi$, even though the bonding seems to be the same as at room temperature.[14] We speculate that at low temperature an extended PLD is not formed because the reduced mobility of the H atoms prevents them from selectively occupying sites that stabilize the $c(2\times2)$ structure. Similarly, the long-range order of this structure is destroyed if the H-atom arrangement is thermally randomized.[39]

In conclusion, we note that an adsorbate-induced reconstruction of the type proposed here probably has been observed in other systems as well. The adsorption of hydrogen on Mo(100)[40] is in many respects similar to that on W(100). Another possible example is W(100)/Cs for which a $c(2\times2)$ structure is also seen[41] but only at an adatom density[42] near ~ 1×10^{14} cm^{-2} so that the apparent conflict between the geometry and the coverage is even greater than for W(100)/H. Apparently Cs is roughly 3 times as effective as H in producing the reconstruction, perhaps because of its greater electropositive character.

[1]E. W. Plummer, in *Interactions on Metal Surfaces*, edited by R. Gomer (Springer, New York, 1975), p. 143.

[2]L. D. Schmidt, in *Interactions on Metal Surfaces*, edited by R. Gomer (Springer, New York, 1975), p. 63.

[3]P. J. Estrup and J. Anderson, J. Chem. Phys. 45, 2254 (1966).

[4]K. Yonehara and L. D. Schmidt, Surf. Sci. 25, 238 (1971).

[5]T. E. Madey, Surf. Sci. 36, 281 (1973); T. E. Madey and J. T. Yates, Jr., *Structure et Propriétés des Surfaces des Solides* (Editions du Centre National de la

Recherche Scientifique, Paris, 1970), No. 187, p. 155.

[6]T. E. Felter, R. A. Barker, and P. J. Estrup, Phys. Rev. Lett. 38, 1138 (1977).

[7]M. K. Debe and D. A. King, J. Phys. C 10, L303 (1977).

[8]R. A. Barker, P. J. Estrup, F. Jona, and P. M. Marcus, Solid State Commun. 25, 375 (1978).

[9]A. Adnot and J. D. Carette, Phys. Rev. Lett. 39, 209 (1977).

[10]The somewhat smaller value obtained by Y. Viswanath, G. Sanders, and L. D. Schmidt, Surf. Sci. 59, 297 (1976), may be due to an overestimate of the oxygen coverage used in the calibration (T. E. Madey, private communication).

[11]D. L. Adams, Surf. Sci. 42, 12 (1974).

[12]T. L. Einstein, Phys. Rev. B 16, 3411 (1977); T. B. Grimley and M. Torrini, J. Phys. C 6, 868 (1973).

[13]J. S. Wang, Proc. Roy. Soc. London, Ser. A 161, 127 (1937); J. K. Roberts, *Some Problems in Adsorption* (Cambridge Univ. Press, Cambridge, England, 1939).

[14]R. A. Barker and P. J. Estrup, to be published.

[15]J. E. Houston and R. L. Park, Surf. Sci. 21, 209 (1970); C. E. Carroll, Surf. Sci. 32, 119 (1972); G. Ertl and J. Küppers, Surf. Sci. 21, 61 (1970).

[16]D. L. Adams and L. H. Germer, Surf. Sci. 23, 419 (1970).

[17]R. Jaeger and D. Menzel, Surf. Sci. 63, 232 (1977).

[18]T. E. Felter and P. J. Estrup, Appl. Surf. Sci. 1, 120 (1977).

[19]H. Froitzheim, H. Ibach, and S. Lehwald, Phys. Rev. Lett. 36, 1549 (1976).

[20]See the discussion by Plummer (Ref. 1) and the references cited therein.

[21]G. W. Rubloff, J. Anderson, M. A. Passler, and P. J. Stiles, Phys. Rev. B 10, 2401 (1974).

[22]M. K. Debe and D. A. King, Phys. Rev. Lett. 39, 708 (1977).

[23]L. C. Feldman and I. Stensgaard, private communication.

[24]E. Tosatti and P. W. Anderson, Jpn. J. Appl. Phys. Suppl. 2, Pt. 2, 381 (1971).

[25]S. E. Trullinger and S. L. Cunningham, Phys. Rev. Lett. 30, 913 (1973).

[26]L. Dobrzynski and D. L. Mills, Phys. Rev. B 7, 2367 (1973).

[27]S. L. Cunningham, W. Ho, W. H. Weinberg, and L. Dobrzynski, Appl. Surf. Sci. 1, 33, 44 (1977).

[28]L. A. Bolshov and A. P. Napartovich, Zh. Eksp. Teor. Fiz. 64, 1404 (1973) [Sov. Phys. JETP 37, 713 (1974)].

[29]R. F. Willis, B. Feuerbacher, and N. Egede Christensen, Phys. Rev. Lett. 38, 1087 (1977); S.-L. Weng, T. Gustafusson, and E. W. Plummer, Phys. Rev. Lett. 39, 822 (1977), and references listed therein.

[30]O. Bisi, C. Calandra, P. Flaviani, and F. Manghi, Solid State Commun. 21, 121 (1977); C. M. Bertoni, C. Calandra, and F. Manghi, Solid State Commun. 23, 255 (1977); S.-L. Weng, Phys. Rev. Lett. 38, 434 (1977); B. Laks and C. E. T. Goncalves de Silva, Solid State Commun. 25, 401 (1978).

[31]N. V. Smith and L. F. Mattheis, Phys. Rev. Lett. 37, 1494 (1976).

[32]K. Terakura, I. Terakura, and Y. Teraoka, in Proceedings of the International Conference on Solid Films and Surfaces, Tokyo, Japan, July 1978 (to be published).

[33]J. E. Inglesfield, J. Phys. C 11, L69 (1978).

[34]E. Tosatti, Solid State Commun. 25, 637 (1978).

[35]J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. 24, 117 (1975); F. J. Di Salvo, Surf. Sci. 58, 297 (1976).

[36]P. Williams, in *Physics and Chemistry of Materials with Layered Structures*, edited by F. Lévy (D. Reidel, Boston, 1976), Vol. 2.

[37]S. C. Moss and R. H. Walker, J. Appl. Crystallogr. 8, 96 (1974).

[38]R. F. Willis and M. Barnes, private communication.

[39]P. J. Estrup, in *Structure and Chemistry of Solid Surfaces*, edited by G. Somorjai (Wiley, New York, 1969), p. 19-1.

[40]C. H. Huang and P. J. Estrup, unpublished results.

[41]A. U. MacRae, K. Muller, J. J. Lander, and J. Morrison, Surf. Sci. 15, 483 (1969).

[42]C. A. Papageorgopoulos and J. M. Chen, Surf. Sci. 39, 283 (1973); H. Jakush, thesis, University of Karlsruhe, 1973 (unpublished); K. Muller, P. Heilmann, K. Heinz, and G. C. Waldecker, Vakuum-Technik 25, 227 (1977).
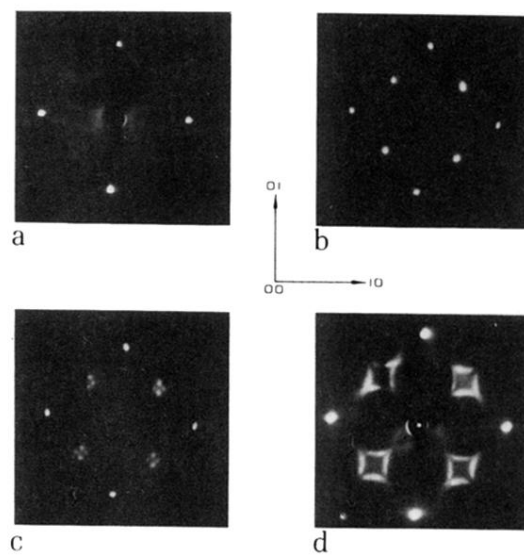
FIG. 2. LEED patterns produced by adsorption of hydrogen on W(100) at room temperature. The primary beam energy is 48 eV. (a) Clean W(100); hydrogen-atom density (b) $\rho \approx 2.5 \times 10^{14}$ cm^{-2}, (c) $\rho \approx 3.7 \times 10^{14}$ cm^{-2}, and (d) $\rho \approx 7 \times 10^{14}$ cm^{-2}.