Finite-size effects on the W(001) low-temperature phase transition

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The W(001) low-temperature, reconstructive phase transition was studied by low-energy electron diffraction with use of a carefully aligned, low-step-density W(001) surface. Finite-size effects on this transition were studied by observing the same transition on a high-step-density W(001) surface which has limited size reconstruction domains of $\sim 60\times 30$ Å. The critical behavior of the step-limited domains shows rounding of the order parameter and shifting of the critical temperature as compared with the results obtained from the much larger flat-surface domains.

The clean W(001) surface has been observed by low-energy electron diffraction (LEED) to have a $(\sqrt{2}\times\sqrt{2})R45°$ structure at temperatures below room temperature.[1,2] It has been proposed that this structure is a result of lateral movement of top-layer W atoms along ⟨110⟩ directions into zig-zag rows,[1] periodic vertical displacements,[3] or a combination of both. The lateral displacement model is preferred from symmetry arguments.[1,4–6] A rapid decrease in superlattice LEED beam intensity as the temperature increases above 200 K is generally associated with a second-order phase transition. In view of recent studies involving the physisorption of krypton on graphite which show that a weakly first-order transition may be easily mistaken for a second-order transition,[7] the assignment for W(001) cannot be considered definite. However, lacking evidence to the contrary, the W(001) phase transition will be treated herein as second order. Symmetry arguments suggest that this transition is a realization of the two-dimensional (2D) *XY* model with cubic anisotropy,[8,9] in which the critical behavior is nonuniversal.[10,11] Monte Carlo and renormalization theoretical studies[12–14] of finite-size effects in the critical region of Ising square lattice and three-state Potts models, as well as the 2D *XY* model with cubic anisotropy, predict that the singularities present in the thermodynamic limit (infinite system) are both rounded and shifted in a finite system, in agreement with scaling theory, as reviewed recently by Barber.[15] These shifted critical values may be regarded as pseudocritical values to differentiate them from their true thermodynamic limits. Few measurements of finite-size effects have been made[15,16] and none have been made on single-crystal surfaces with controlled domain sizes.

To observe the predicted finite-size effects, we have prepared two W(001) surfaces; one is a flat surface [within 0.1° of the (001) orientation], and the other is a high-step-density surface [3.25° ± 0.25° off the (001) orientation], with step edges parallel to the [010] and an average terrace width of ~ 30 Å [Fig. 1(d)]. Details of the crystal preparation, mounting, and cleaning are given elsewhere.[5] Reconstruction occurs on the high-step-density surface, but the domain size is limited, or controlled, by the terrace width.[5,17–19] In this paper, we report and compare experimental low-energy electron diffraction results for the phase transition of the flat and stepped surfaces which reveal pronounced finite-size effects.

The LEED patterns observed with a backviewing screen[20] from these surfaces at room temperature (with a background pressure $< 3\times 10^{-11}$ Torr to reduce H contamination) contain only integral-order beams. In the case of the stepped surface, at certain energies these beams are split perpendicular to the step edge direction,[21] as shown in Fig. 1(c). Detailed measurement of this splitting was obtained with an electron spectrometer,[22] with angular and energy resolutions of 0.6° and 25 meV, respectively. Integral-order beam splitting from the stepped surface indicated an average step separation of 30 ± 2 Å, while the lack of any splitting or measurable oscillation in beam width versus energy from the flat surface permits a lower bound of 400 Å to be established for the terrace width of the flat surface.[17]

When the crystal is cooled to 100 K, half-order beams due to surface reconstruction appear, as shown in Figs. 1(a) and 1(c). The $\{\frac{1}{2},\frac{1}{2}\}$ beams on the stepped surface are elongated perpendicular to the steps in contrast to the smaller, round $\{\frac{1}{2},\frac{1}{2}\}$ beams observed with the flat surface. The superlattice beam shapes indicate the shapes of the reconstruction domains on the surface,[5,17,18] while the presence of all four $\{\frac{1}{2},\frac{1}{2}\}$ beams for surfaces with nearly equal in-

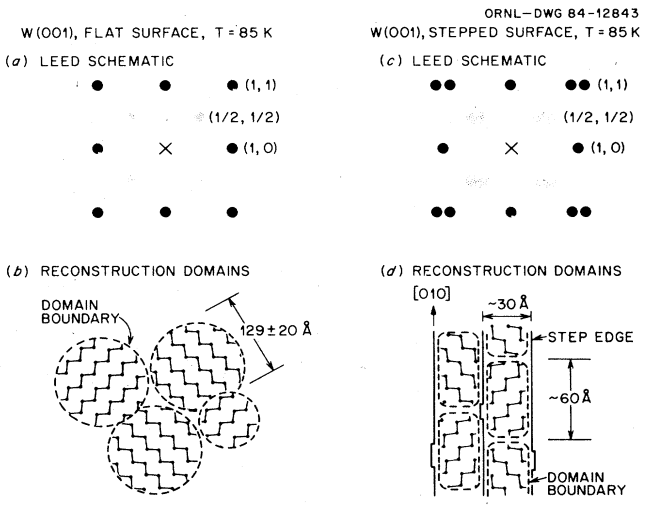

FIG. 1. Schematics of LEED patterns observed with flat and stepped surfaces below T_c and the sizes and shapes of reconstruction domains determined from detailed angular measurements of $\{\frac{1}{2},\frac{1}{2}\}$ beams. The lateral atomic displacements indicated for the zig-zag model are highly exaggerated.

tensities implies that both of the domain orientations possible are present in nearly equal numbers.[1] From the measured 2D angular intensity distributions (deconvoluted from the instrumental broadening to get the physical broadening $\Delta\theta$), the average domain size M was determined in two perpendicular directions by using $M = 0.888\lambda/(\Delta\theta\cos\theta)$, where λ is the electron energy wavelength and θ is the diffraction angle.[19] The maximum average domain dimensions determined for the lowest obtainable sample temperature are indicated in Figs. 1(b) and 1(d). There is, in reality, a distribution of both terrace widths and domain dimensions, but only average values are represented here. The short dimension of the stepped surface domains corresponds closely to the average terrace width and the long dimension is less than half that of the flat surface domain width. Most significant for the present study, this results in an average domain area ratio of $\sim 1{:}8$ for the stepped versus flat surfaces, which provides the controlled size difference desired for observation of finite-size effects. A serious concern, though, is that shape effects due to the more rectangular shape of the stepped surface domains may seriously influence the results. However, recent calculations by Kleban, Akinci, Hentschke, and Brownstein[23] indicate that for an aspect ratio less than 2, the critical behavior of a rectangular domain is very similar to a round domain.

The temperature dependence of the $(\frac{1}{2},\frac{1}{2})$ beam peak intensity $I(T)$ was observed while the crystal was cooling after either high-temperature flashing (~ 2000 K) to remove oxygen or after mild heating (~ 450 K) to remove hydrogen, as well as at several fixed temperatures. As observed before,[1-3,24] the half-order beams have some intensity at temperatures well above room temperature, which is associated with short-range order as discussed below. The data obtained are independent of cooling rate, reversible with temperature, and continuous to within experimental resolution; i.e., the data are consistent with a second-order phase transition. To remove the Debye-Waller effect from the data, the $I(T)$ curves were normalized to the Debye-Waller slope estimated from the data obtained below the transition temperature on the flat surface. These $I_N(T)$ values for the flat surface shown in Fig. 2(a) remain near 1 for a small temperature range and then rapidly drop in the vicinity of a critical temperature T_c. In contrast, the integral-order beam intensities increase slightly near T_c; these increases reflect a redistribution of intensity in the entire reciprocal space, after which typical Debye-Waller temperature-dependent decay is observed. For $T < T_c$, $I_N(T)$ obtained from small, step-limited domains is lower than the $I_N(T)$ obtained from large domains, and the reverse is true when $T > T_c$. Thus, $I_N(T)$ (which is proportional to the square of the order parameter) is more rounded for a smaller domain size, an observation in qualitative agreement with the theoretical results already discussed.

The temperature dependencies of the full width at half maximum (FWHM) of the $(\frac{1}{2},\frac{1}{2})$ beams have also been measured and are shown in Fig. 2(b). The broadening of these beams, coincident with the rapid decay in peak intensity as reported previously for surfaces with large terrace widths,[1,3,24] implies a decrease in domain size to a diameter of ~ 12 Å independent of whether the surface is flat or stepped. This short-range order is not necessarily associated with static domains, but may be transitory in nature. The existence of short-range order for $T > T_c$ is consistent with

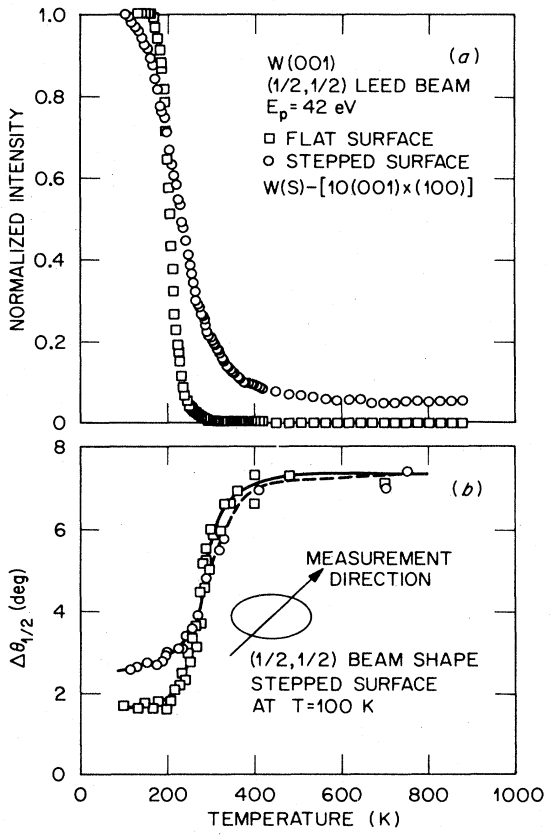

FIG. 2. (a) Normalized $(\frac{1}{2},\frac{1}{2})$ LEED beam intensities for flat and stepped surfaces as a function of temperature. The intensities were normalized to the Debye-Waller slope of the flat surface $(\frac{1}{2},\frac{1}{2})$ beam intensity below T_c. (b) Measured FWHM of the $(\frac{1}{2},\frac{1}{2})$ beams for both flat and stepped surfaces as a function of temperature.

Monte Carlo and renormalization-group studies on the W(001) surface[25] and also with the experimental results of ion scattering,[26] and may explain the conflict between theory and photoemission experiments.[27] An alternate suggestion by King[6] is that the reconstruction is nucleated from the upper step edges for a distance which decreases with temperature. On a high-step-density surface, more of the surface would then be reconstructed at high temperature than on the nearly flat surface. At present, we cannot distinguish from the angular profiles whether the surface is indeed divided into two different structures by steps, but it is consistent with the higher $(\frac{1}{2},\frac{1}{2})$ beam intensities observed here for the stepped versus flat surfaces at $T >> T_c$. A more detailed understanding of half-order beams at high T will help to elucidate the (long-range) order-order versus order-disorder nature of the transition.

The rounding of $I_N(T)$ near the transition temperature and the shifting of the transition temperature due to finite-size domains can be quantified in terms of a second-order phase transition. Utilizing the procedures applied by Lyuksyutov and Fedorus[28] to the H-W(001) phase transition, we can extract the critical exponent β and critical temperature T_c from the critical region of the W(001) system. First, the

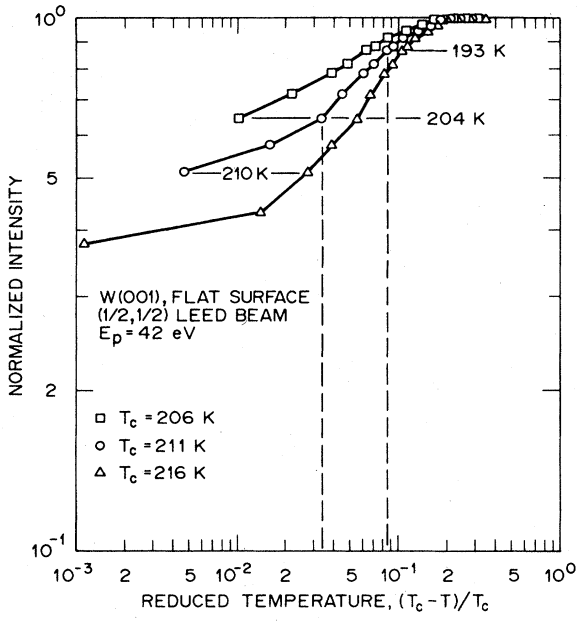

FIG. 3. Log-log plot of normalized intensity vs reduced temperature for several assumed values of T_c for the flat surface. The dotted lines indicate the region within which the best fit to a straight line, i.e., power-law behavior, is obtained for $T_c = 211$ K.

critical region is examined by plotting the temperature dependence of the $(\frac{1}{2},\frac{1}{2})$ beam intensity versus reduced temperature in logarithmic coordinates at different values of the adjustable parameter T_c as shown in Fig. 3 (flat surface). For an infinite system, the phase transition should be described by a power law of the form $I = I_0[(T_c - T)/T_c]^{2\beta}$ in the critical region. As a result of finite-size effects, the critical temperature region to which the power law applies is below and separated from T_c. Accordingly, the power law may be reformulated[28,29] as

$$I = [I_0/(2\pi)^{1/2}\Delta t]\int_{T-T_c}^{\infty}\left[\frac{T_c - T + t}{T_c + t}\right]^{2\beta}\exp\left[-\frac{1}{2}\left[\frac{t}{\Delta t}\right]^2\right]dt \ ,$$

where ΔT describes the transition temperature "smearing" width,[28] which is related to the domain size and size distribution. As can be seen in Fig. 3, the critical region, and hence β, depends on the choice of T_c. If T_c is chosen as 211 K on the flat surface, the intensity data in the range $T_c - 17$ to $T_c - 6$ are consistent with the power law. The "best-fit" values of T_c and β were determined through a four parameter $(T_c, \beta, I_0, \Delta t)$ fit using Horn's power-law formulation and a range of assumed critical temperature regions. Optimal values of T_c, β, I_0, and Δt were thus determined to be 211, 0.144 ± 0.04, 1.76, and 3.26 K for the flat surface and 217, 0.050 ± 0.01, 0.95, and 2.32 K for the stepped surface, respectively. The error limits indicated for β were obtained by assuming a ± 5 K error in T_c, but since the errors are likely to be in the same direction for both surfaces, the qualitative comparison should not be affected. In each case calculated $I_n(T)$ curves using the best-fit parameters are virtually indistinguishable from the measured $I_n(T)$ (Fig. 2) for $T < T_c$.

In conclusion, two W(001) surfaces with different step densities which provided two distinct size distributions of reconstruction domains were prepared. This allowed the study of finite-size effects on the critical behavior of the W(001) phase transition, providing the first experimental observation on a single-crystal surface of the finite-size effects predicted for surface phase transitions. The critical exponent β and the critical temperature were found to have different values for different domain sizes and the anticipated rounding of $I(T)$ for smaller domains was observed.

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[1]M. K. Debe and D. A. King, Phys. Rev. Lett. **39**, 708 (1977); Surf. Sci. **81**, 193 (1979).
[2]T. E. Felter, R. A. Barker, and P. J. Estrup, Phys. Rev. Lett. **38**, 1138 (1977).
[3]R. T. Tung, W. R. Graham, and A. J. Melmed, Surf. Sci. **115**, 576 (1982); A. J. Melmed, R. T. Tung, W. R. Graham, and G. D. W. Smith, Phys. Rev. Lett. **43**, 1521 (1979); A. J. Melmed and W. R. Graham, Appl. Surf. Sci. **11-12**, 470 (1982).
[4]D. P. Woodruff, Surf. Sci. **122**, L653 (1982).
[5]J. F. Wendelken and G.-C. Wang, J. Vac. Sci. Technol. A **2**, 888 (1984).
[6]D. A. King, Phys. Scr. **T4**, 34 (1983).
[7]E. D. Specht, M. Sutton, R. J. Birgeneau, D. E. Moncton, and P. M. Horn, Phys. Rev. B **30**, 1589 (1984).
[8]P. Bak, Solid State Commun. **32**, 581 (1979).
[9]K. Binder, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1983).
[10]J. V. Jose, L. P. Kadanoff, S. Kirkpatrick, and D. R. Nelson, Phys. Rev. B **16**, 1217 (1977).
[11]E. Domany and E. K. Riedel, Phys. Rev. Lett. **40**, 561 (1978).
[12]D. P. Landau, Phys. Rev. B **13**, 2997 (1976).
[13]S. C. Ying and G. Y. Hu (private communications).
[14]A. N. Berker and S. Ostlund, J. Phys. C **12**, 4961 (1979).
[15]M. N. Barber, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1983).
[16]R. J. Birgeneau, P. A. Heiney, and J. P. Pelz, Physica **109-110B+C**, 1785 (1982).
[17]J. F. Wendelken and G.-C. Wang, Surf. Sci. **140**, 425 (1984).
[18]G.-C. Wang and T.-M. Lu, Surf. Sci. **122**, L635 (1982).
[19]T.-M. Lu and G.-C. Wang, Surf. Sci. **107**, 139 (1981).
[20]J. F. Wendelken, S. P. Withrow, and P. S. Herrell, Rev. Sci. Instrum. **51**, 255 (1980).
[21]J. M. Pimbley and T.-M. Lu, J. Appl. Phys. **55**, 182 (1984).
[22]J. F. Wendelken and F. M. Propst, Rev. Sci. Instrum. **47**, 1069 (1976).
[23]P. Kleban G. Akinci, R. Hentschke, and K. A. Brownstein, J. Phys. A (to be published).
[24]P. Heilmann, K. Heinz, and K. Muller, Surf. Sci. **89**, 84 (1979).
[25]L. D. Roelofs, G. Y. Hu, and S. C. Ying, Phys. Rev. B **28**, 6369 (1983).
[26]I. Stensgaard, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. **42**, 247 (1979).
[27]L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **29**, 5372 (1984).
[28]I. F. Lyuksyutov and A. G. Fedorus, Zh. Eksp. Teor. Fiz. **80**, 2511 (1981) [Sov. Phys. JETP **53**, 1317 (1981)].
[29]P. M. Horn, R. J. Birgenau, P. Heiney, and E. M. Hammonds, Phys. Rev. Lett. **41**, 961 (1978).