

Order-Disorder Transition of the W(001) Surface

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Synchrotron x-ray diffraction has been used to study the surface reconstruction of W(001) through its phase transition at around 230 K. We find that, although the superlattice peak intensity decreases a thousandfold over the range studied, the integrated intensity, and hence the structure factor, is nearly constant. This indicates that the surface undergoes an order-disorder transition with little change in the magnitude of the atomic displacements. The critical behavior is compared with predictions of the 2D XY and Ising models.

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The reconstruction of the clean W(001) surface at low temperatures has been widely studied since its discovery by low-energy electron diffraction (LEED).^{1,2} Below ~ 200 K, a well-defined $(\sqrt{2} \times \sqrt{2})R45^\circ$ phase exists whose basic structure³ is no longer seriously disputed, although certain details are still emerging.⁴ The nature of the high-temperature (HT) (1×1) phase has been investigated experimentally and described as a disordered version of the low-temperature (LT) phase,⁵ an ordered state,^{6,7} perhaps with a lower-symmetry (1×1) reconstruction,⁸ or, just recently, an incommensurate phase.⁹ Several groups have investigated the phase transition with LEED^{2,10-12} and He diffraction.^{9,13} Theoretical work on the phase transition has also been divided between order-order and order-disorder models.¹⁴⁻¹⁹

The belief that there is a change of structure associated with this phase transition rests almost entirely on the LEED reports of a large drop in intensity of the half-order diffraction beams above 200 K.^{2,10-12} In this paper we wish to qualify this basic experimental fact, by reporting that the kinematical x-ray diffraction intensity is nearly *constant* throughout the entire temperature region 130–360 K and that above the transition temperature T_c the peak merely changes shape to conserve its volume. Since there is no change in structure factor, the local structure is unaltered through the transition and so the HT phase must be *disordered*. By measuring the peak widths as a function of T , we find that as the ordered domains diminish in size they retain an anisotropic 2:1 axial ratio. The peak widths scale approximately linearly with $T - T_c$, consistent with the classification of the phase transition as a 2D XY model with strong cubic anisotropy.^{16,17} Furthermore, we see no shift of the peak centroid from the true half-order position over 130–360 K, and thus no sign of incommensurability.

To make a definitive association between the intensity of a diffraction feature and the correlation function in a phase transition, it is essential to be sure of kinematical scattering conditions. At the same time we must use a probe that scatters strongly enough to detect a monolayer of atoms at a surface. X rays are the ideal compromise here, and the advent of synchrotron radiation sources has made such experiments practical.

Our experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline VII-2 using focused monochromatic radiation of 1.3-Å wavelength. Glancing-incidence geometry was used to measure the diffracted intensity at reciprocal points (hkl) with $l=0.1$ corresponding to an incidence angle of 1.2° . The sample was mounted inside an ion-pumped vacuum system⁴ at the center of a four-circle diffractometer operating with $\omega=0$. Si(111) monochromators and a 4×4 -mm² exit slit provided a resolution of 0.007 Å⁻¹ FWHM. The sample was a ribbon $0.25 \times 9 \times 30$ mm³ oriented to $(001) \pm 0.5^\circ$. Sample temperatures between 150 and 2500 K, obtained with a combination of liquid-nitrogen cooling and resistive heating, were measured with a (W-5% Re)-(W-25% Re) thermocouple and corrected for resistive offset. Initial cleaning was achieved with cycles of flashing to 2300 K and annealing to 1400 K in 1×10^{-7} Torr O₂.⁴ The sample was re-cleaned before every scan by flashing twice to 2000 K, then cooling to the measurement temperature. Over a long period of time, changes in the half-order diffraction intensity and line shape due to contamination could be observed, but this effect was negligible during a 20-min scan. This was checked by cooling after every data point.

Figure 1 shows the atomic arrangement in one of the two possible orientations of the LT $(\sqrt{2} \times \sqrt{2})$ structure

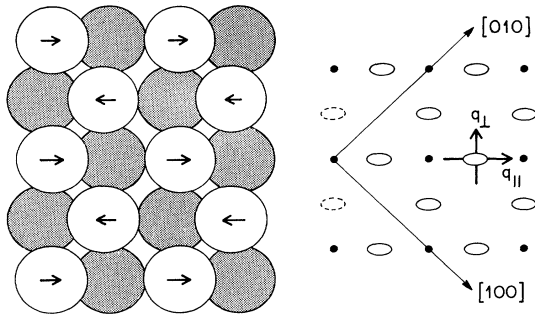


FIG. 1. Atomic model and diffraction pattern of the low- T ($\sqrt{2} \times \sqrt{2}$) reconstruction of W(001). Bulk diffraction peaks, e.g., (000), (020), (110), and (200), are solid circles, and the half-order peaks unique to the reconstructed layer are ellipses. Integer-order surface peaks are not shown. Top-layer atoms (unshaded) are displaced as indicated to form zig-zag chains oriented up and down in the figure. The displacements of the second-layer atoms⁴ (shaded) are not shown. This structure gives rise to a nodal line of surface peaks with zero structure factor (dashed ellipses). Other regions of the surface have the displacements up and down and the chains left to right. These regions do not contribute to the diffraction at $(\frac{3}{2}, \frac{3}{2}, 0)$ where the measurements were made: q_{\perp} and q_{\parallel} define the transverse and radial scan directions employed.

and its diffraction pattern. A rotation by 90° gives the other possible structure and its diffraction pattern. The symbols q_{\parallel} and q_{\perp} indicate the direction of scans that independently probe correlations parallel to and perpendicular to the atomic displacements in the structure shown in the figure. Representative scans at various temperatures are shown in Fig. 2. The solid curves are convolutions of the experimental resolution function with the sum of a constant background B and a 2D Lorentzian²⁰

$$L(q_{\parallel}, q_{\perp}) = A / (1 + \xi_{\parallel}^2 q_{\parallel}^2 + \xi_{\perp}^2 q_{\perp}^2). \quad (1)$$

Here $q_{\parallel} = Q_{\parallel} - Q_{\parallel 0}$ and $q_{\perp} = Q_{\perp} - Q_{\perp 0}$ are the deviations of momentum transfer $(Q_{\parallel}, Q_{\perp})$ from the half-order peak at $(Q_{\parallel 0}, Q_{\perp 0})$ shown in Fig. 1, and ξ_{\parallel} and ξ_{\perp} are the correlation lengths in the corresponding directions. The resolution function was measured at the bulk (110) peak and included the effects of the surface mosaic, which gave rise to bimodal line shapes in the lowest-temperature q_{\perp} data. Apart from the angular separation of these two mosaic grains, the resolution was significantly sharper than the peaks.²¹

Six fit parameters, A , B , ξ_{\parallel} , ξ_{\perp} , $Q_{\parallel 0}$, and $Q_{\perp 0}$ were this evaluated at each temperature. $Q_{\perp 0}$ was always, within error, equal to zero, and B showed only a gradual 20% increase with temperature over the entire range, which can be attributed to bulk thermal diffuse scattering; the remaining parameters are plotted in Fig. 3. Dramatic changes of 3 orders of magnitude in A and 1.5 orders in ξ_{\parallel} and ξ_{\perp} are clearly evident. Qualitatively the variations are in agreement with LEED and He-atom diffraction data.⁹⁻¹³ However, the x-ray measurements

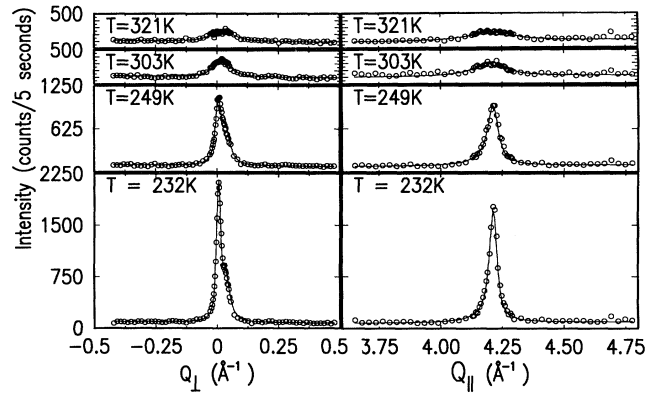


FIG. 2. Radial (Q_{\parallel}) and transverse (Q_{\perp}) momentum transfer profiles of the $(\frac{3}{2}, \frac{3}{2}, 0)$ surface peak at various temperatures in the transition region.

show that these changes almost exactly compensate each other in the integrated intensity,²¹ where the integration is over the Brillouin zone:

$$A_1 = \int \int_{-a^* \sqrt{2}/4}^{a^* \sqrt{2}/4} L(q_{\parallel}, q_{\perp}) dq_{\parallel} dq_{\perp}, \quad (2)$$

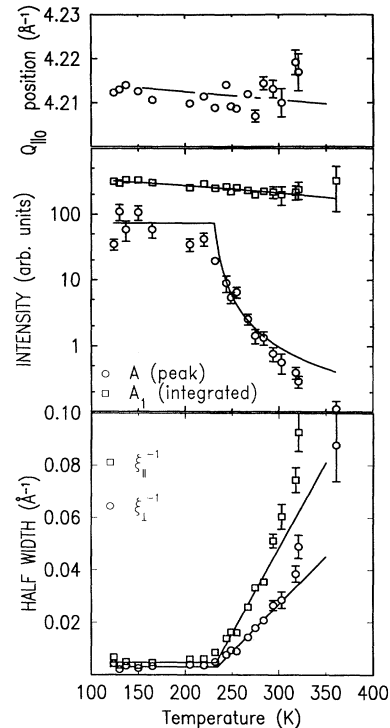


FIG. 3. Line shape fitting parameters ξ_{\parallel} , ξ_{\perp} , A , and $Q_{\parallel 0}$ together with A_1 derived from Eq. (2) as functions of temperature. In the top panel the straight line gives the predicted position of Q_{\parallel} at $(\frac{3}{2}, \frac{3}{2}, 0)$ using a W lattice parameter $a_0 = 3.16 \text{ \AA}$ and a thermal expansion coefficient of $4.4 \times 10^{-6} \text{ K}^{-1}$. In the two lower panels the lines through the data are Eqs. (3) and (4) discussed in the text.

where $a^* = 1.99 \text{ \AA}^{-1}$ is the reciprocal-lattice parameter. A_1 is essentially flat over the entire range 130 to 360 K. The slope indicates a surface vibration amplitude of $\langle u_z^2 \rangle^{1/2} = 0.19 \pm 0.07 \text{ \AA}$ at 300 K according to the Debye theory²²; this compares with a bulk value of 0.042 \AA .²² With only one diffraction order, we cannot distinguish an alternative explanation of the T dependence of A_1 , that the magnitude of the atomic displacements in the top layer decreases with T ; the upper limit would be 20% over the entire range because of the quadratic coupling with intensity.⁴ In either case, the present result that the integrated intensity is nearly conserved proves that the transition is order-disorder type.

The order-disorder model provides a picture of the surface structure at temperatures above the phase transition of fluctuating $\sqrt{2} \times \sqrt{2}$ domains with average dimension $\xi_{\parallel} \times \xi_{\perp}$ separated by domain walls which may take a variety of forms. For example, a simple antiphase boundary consisting of one or more lines of W atoms without displacements, or with displacements different from the $\{110\}$ directions, may be appropriate.^{17,19,23} However, broad domain walls of the first kind with substantial surface area are not compatible with the observed $A_1(T)$. The axial ratio $\xi_{\parallel}/\xi_{\perp}$ of the domain size is constant at 0.5 ± 0.1 above the transition, in the temperature range 230 to 360 K, even though the ξ 's themselves change thirtyfold. This ratio is believed to reflect the relative energy cost of domain walls parallel to the bonded chains (up and down in Fig. 1) and across chains; walls are favored along the chains as expected.²¹ The constancy of the ratio with temperature is also expected from scale invariance of 2D critical phenomena.

Below T_c the correlation lengths are constant but still in roughly the same 1:2 ratio. Here the domain size ($\sim 200 \text{ \AA}$) is of the same order of magnitude as the spacing between steps due to the sample miscut. We suspect therefore that the behavior is no longer intrinsic to W(001). We looked carefully for a change of line shape below T_c as evidence of random-field effects,²⁴ without results of significance. On deliberately miscut crystals, different domain aspect ratios can be achieved below T_c , as has been seen with LEED,¹² but effects above T_c do not appear to have been investigated systematically.

Symmetry considerations classify this phase transition as a 2D XY model with cubic anisotropy, assuming atomic displacements of constant magnitude along directions specified by the order parameter.¹⁶ In the limit of infinitely large anisotropy, permitting displacements only along the four $\{110\}$ directions (see Fig. 1), the model simplifies into two decoupled 2D Ising models, one for each domain orientation.¹⁶ Monte Carlo simulations of the critical fluctuations with finite anisotropy have demonstrated the crossover from XY to Ising.¹⁷ We compare our data first with predictions of the 2D Ising model, given by the solid lines through the A , ξ_{\parallel} , and ξ_{\perp} data

in Fig. 3:

$$A(T) = TA_0(T - T_c)^{-\gamma}, \quad T > T_c, \quad (3)$$

$$\xi(T) = \xi_0(T - T_c)^{-\nu}, \quad T > T_c, \quad (4)$$

with $\gamma = 1.75$ and $\nu = 1$. We have used the fact that Eq. (4) is a straight line in our plot to establish the value of $T_c = 230 \text{ K}$. Below T_c , there should be a sharp 2D Bragg peak as well as diffuse scattering, but our line shape remained Lorentzian presumably because it was extrinsically pinned, so we were not able to distinguish these. In previous LEED studies of the $T < T_c$ region the exponent β has been found to be 0.146 ¹² which compares with the Ising value of 0.125 .

As seen in Fig. 3, the agreement of the x-ray results with the 2D Ising model is reasonable in the range 230–300 K close to the transition, but deviates at large T . The sign of the deviation indicates $\nu > 1$, $\gamma > 1.75$, which is consistent with a Monte Carlo simulation study of the 2D XY model with finite cubic anisotropy¹⁷; this model has nonuniversal behavior with diverging ν as the anisotropy field approaches zero.^{17,25} We cannot establish whether or not this model is appropriate because the temperature may be outside the range of validity of the scaling hypothesis. Finally we note that the T dependence of the peak position $Q_{\parallel 0}$ at the top of Fig. 3 is within error of the thermal expansion coefficient of W (straight line in Fig. 3), and consistent with the simple domain-wall disordering model of the phase transition. The behavior is *inconsistent* with the result of He scattering that the half-order diffraction peak shifts by 15% at 320 K,^{9,13} and with the interpretation of an incommensurate HT structure.⁹

We would like to point out in conclusion that we have observed and interpreted the diffuse x-ray scattering from fluctuations in a single layer of atoms more than 100 K above a second-order phase transition, where the intensity fills a substantial fraction of the Brillouin zone. This demonstrates that investigation of surface phase transitions from the poorly correlated to the critical regimes with synchrotron x-ray diffraction is viable. The W(001) ($\sqrt{2} \times \sqrt{2}$)-to-(1×1) phase transition is shown to be order-disorder type with little change of local structure. The half-order surface diffraction peak does not “disappear” above the transition; it simply spreads out in a manner consistent with the predictions of the 2D XY model with strong anisotropy.¹⁷

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