# Non-Ising Behavior of the Pt(110) Surface Phase Transition

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We have investigated the structural transition of the Pt(110)1×2 reconstruction using x-ray diffraction. We find weakening and broadening of the half-order peak with temperature above $T_c = 1080$ K, exactly analogous to the Au(110)1×2 surface studied by LEED. Unlike the Au(110) result, however, we find the peak shifts as well, indicating that steps spontaneously appear in Pt(110) above $T_c$. Even though we find good agreement with theoretical 2D Ising exponents, the steps refute classification of this system as a simple two-state model, and favor a roughening description instead.

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Phase-transition theory makes strong predictions for second-order transitions in two dimensions (2D), not the least of which is the exact solution of the 2D Ising model by Onsager.[1] Experimentalists have long sought "ideal" examples of 2D phase transitions to test the theories, and recently one such case, the Au(110) reconstructed surface, has been reported.[2] At low temperature this surface has an ordered 1×2 state with a "missing-row" structure[3] in which alternate rows of top-layer sites are occupied or vacant. The half-order low-energy-electron-diffraction (LEED) peak that characterizes this structure was seen to change shape with temperature and was analyzed in terms of an order parameter diminishing as $(T_c - T)^{2\beta_c}$ with $\beta_c = 0.13 \pm 0.02$, and then replaced by critical scattering near the transition at $T_c = 650$ K. This was not only consistent with the predictions of the 2D Ising model, but rational, since top-layer atoms can sit in one of two possible sites.[4]

The surface of Pt(110) has the same 1×2 missing-row reconstruction as Au(110).[5] Total-energy calculations[6,7] also favor the missing-row model and indicate considerable similarity between the Pt and Au structures. It has been argued by several authors,[7-9] however, that the missing-row configuration is only marginally stable with respect to the formation of steps since these incorporate simple extensions of the (111) microfacets making up the reconstruction. Indeed, Villain and Vilfan[8] have predicted that Au(110) should roughen by spontaneous formation of such facets at a temperature somewhat above its Ising transition. Thermal roughening of non-close-packed metal surfaces is itself a subject of great interest because it is expected on theoretical grounds;[10] above the roughening temperature the height-height correlation function should diverge logarithmically and give rise to a power-law line shape, as has been recently observed on Ag(110).[11] Monte Carlo methods[12] have also been used to simulate the Au(110) phase transition as a 2D Ising model. This agrees well with the experiment[2] and predicts the same behavior for Pt(110) with $T_c = 750$ K. The only experimental evidence of a phase transition in Pt(110) is a slight core-level shift seen in photoemission at $940 \pm 50$ K analogous to the same effect in Au(110) at $620 \pm 40$ K.[13]

Here we report x-ray-diffraction results for the Pt(110) phase transition, which we observe at $T_c = 1080 \pm 50$ K. In many ways we find similar behavior to Au(110),[2] with one important difference: Above $T_c$ steps are created spontaneously and their density diverges with temperature. Because step proliferation is found to be a central component of the disorder above $T_c$, the transition must therefore be classified as a *roughening* transition and not a simple two-state 2D Ising transition.

We chose to study Pt(110) because we found it to be intrinsically better ordered than Au(110). Considerable care was required with surface preparation to reach this high degree of order for the starting surface. First, C impurities were removed by extensive treatment at 1200 K in $10^{-6}$ Torr $O_2$. C was found to lead to a structure that was locally 1×1, as evidenced by diffraction intensity at the in-plane (1,0,0) crystal truncation rod that happens to have nearly zero intensity for the ideal 1×2 structure. This signature was at least 10 times more sensitive than Auger spectroscopy for detection of C. Even the clean surface in $1 \times 10^{-10}$ Torr was not well ordered until a long series of anneals, gradually raising temperature over an 8-h period, was performed. Temperature was measured with a thermocouple spot welded to the sample, which limited the absolute accuracy. X-ray-diffraction measurements were then made in the same vacuum system using the four-circle diffractometer[14] at beam line X16A of the National Synchrotron Light Source (NSLS). Resolution was determined by 2×10-mm slits at 500 mm on the $2\theta$ arm, corresponding to 0.02 $Å^{-1}$ FWHM.

We found that Pt(110) has exactly the same pattern of shifted half-order diffraction peaks as Au(110), which is explained in terms of randomly distributed single-height steps on the surface.[15] Fenter and Lu[16] considered the general case of diffraction from surfaces containing this kind of disorder and concluded that the peak shift should *oscillate* as a function of perpendicular momentum transfer, $l$. This highly unusual behavior requires a change in height at the active defect between or-

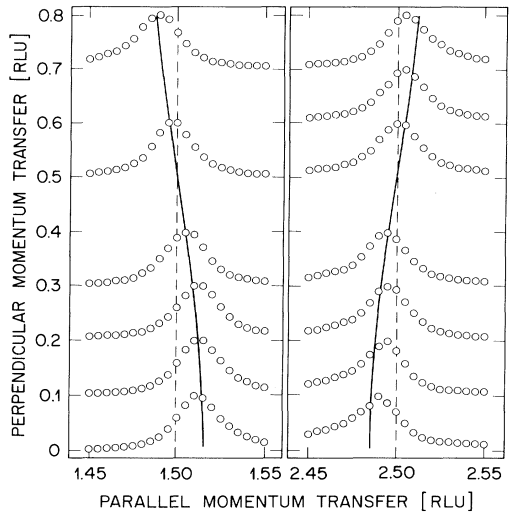


FIG. 1. The solid line is the locus of the half-order superstructure peak positions for Pt(110) at room temperature before the sample was fully annealed. The oscillatory shift of $h_{max}$ from the exact half-order value as a function of $l$ is taken from the theory of Fenter and Lu (Ref. 16). Superimposed are x-ray diffraction scans, normalized to unit height, at $(hll)$ for $h$ near 1.5 (left) and $h$ near 2.5 (right) and $0.1 \leq l \leq 0.8$ reciprocal lattice unit (RLU) in the conventional cubic (Miller index) coordinate frame.

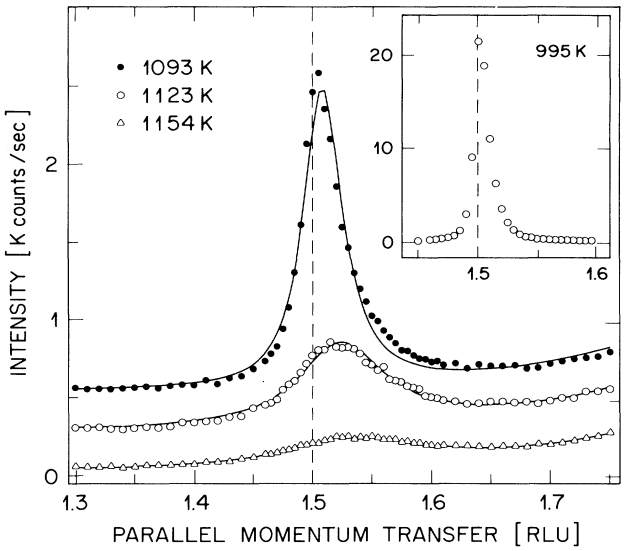


FIG. 2. Temperature dependence of the half-order line shape at $(h,0.06,0.06)$ obtained by scanning $h$. Thermal expansion of the crystal has been corrected by adjustment of the lattice-parameter values, and the ordinates are offset for clarity. Inset: $T < T_c$ line shape, on a different vertical scale, which was used to obtain the fits shown for $T > T_c$ by numerical convolution with a Lorenzian. The shift of the peak to larger $h$ as the line broadens with $T$ is clearly apparent.

dered domains because the phase shift must change sign with $l$. We found exactly this behavior, shown in Fig. 1, and concluded that the step model must be correct for Pt(110). It is interesting to note that the high-resolution LEED measurements of the Au(110) line shape,[2] which did not see a shift, were made under diffraction conditions that correspond to $l \simeq 0.5$ in Fig. 1, where the shift is zero.

The principal result of this paper is that this peak shift is also temperature dependent as Fig. 2 shows. After careful annealing, our sample gave the line shape shown in the inset. Although resolution limited in the center, the peak is still shifted slightly and has a distinct tail on the high-$q$ side, revealing a residual step distribution in the surface. However, at $T > T_c$ the peak broadens and *shifts* dramatically and completely reversibly; it also broadens at about 25% of the rate in the transverse direction (data not shown). It is apparent, in view of the relation between steps and peak shift,[15,16] that an equilibrium density of steps appears spontaneously above $T_c$, and hence that the phase transition is also a roughening transition.

In attempting to fit the detailed peak shapes of Fig. 2, we found all the previous models[4,10,15,16] to be inadequate. We therefore constructed a more general model of the surface disorder shown in Fig. 3 that contains both randomly distributed steps with a total probability $\alpha$ and also antiphase boundaries with a total probability $\beta$. Of the six possible microscopic excitations of the missing-row structure considered by Villain and Vilfan,[8] the four cases shown are determined to be the most energetically favorable.[9] The remaining cases[8] could be readily added, but give rise to peak shifts in the *wrong* direction,

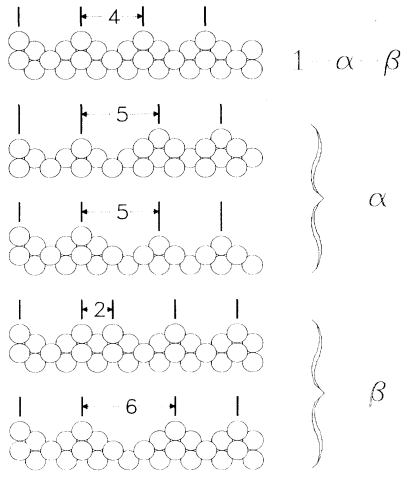


FIG. 3. Side view of the ideal missing-row model of the structure of the $1\times2$ Pt(110) surface (top) and four low-energy excitations containing different line defects that could appear as microscopic fluctuations of the surface state. The parallel phase shift, in units of $a_0/2$, between adjacent $1\times2$ regions is indicated, along with the combined probabilities of the groups of related defects assumed in calculating the diffraction line shape.

and so have been omitted. These are also the predominant defects seen in scanning-tunneling microscopy of Au(110) and Pt(110).[17] When $\beta=0$ our model degenerates to the random-step model.[15,16] When $\alpha=0$ it becomes a planar two-state description of the surface, identical to that predicted by the 2D Ising model,[4,12] as used in the construction of the Monte Carlo model of Daw and Foiles[12] which explicitly prohibited the appearance of steps.

We will now derive the shape of the diffraction predicted by this one-dimensional model. While it should be possible to generalize the derivation of Fenter and Lu,[16] we use a new approach that is much simpler. The defects are assumed rare and noninteracting so the probabilities $\alpha$ and $\beta$ are small and independent, but are expected to change with temperature. We need to consider only the effect of the defects on the spacing of neighboring top-layer atoms, as shown in Fig. 3. If $\rho(x)$ is the occupation probability of a site $x$, measured in half-cell spacings $a_0/2$, then the correlation function, $C_x=\langle\rho(x)\rho(0)\rangle$, satisfies the recurrence relation

$$C_{x+5}=\beta C_{x+3}+(1-\beta-\alpha)C_{x+1}+\alpha C_x .$$

The general solution can be written down to first order in $\alpha$ and $\beta$,

$$C_x=\sum_{j=1}^{5} a_j \epsilon_j^{|x|}, \quad \epsilon_2=\alpha/2-1 ,$$

$$\epsilon_{1,3}=\alpha/4\pm(1-\beta/2-\alpha/4)i ,$$

where the $a_j$ coefficients are determined by boundary conditions and $\epsilon_{4,5}$ are uninteresting here. The diffracted intensity is the Fourier transform of $C_x$,

$$I(q)=\sum_{-\infty}^{\infty} C_x e^{iqx}$$

$$=\sum_{j=1}^{5} a_j\left(\frac{1}{1-\epsilon_j e^{iq}}+\frac{1}{1-\epsilon_j e^{-iq}}-1\right).$$

For $\alpha\ll 1$, $\beta\ll 1$, this has a Lorenzian shape with peaks centered at $q_j$ of half-width $w_j$ given by

$$q_{1,3}=\pm(\pi/2-\alpha/4), \quad w_{1,3}=\beta/2+\alpha/4 ,$$

$$q_2=\pi, \quad w_2=\alpha/2 .$$

The (1.5,0,0) peak we measured is at $q=q_3$ with shift of $\alpha/4$ and a half-width of $\beta/2+\alpha/4$. It is clear that the shift is due only to the steps, whereas the width can be associated with either steps or antiphase defects. The sense of the steps, up or down, is unimportant for in-plane diffraction, since both led to the same difference in phase across the defect. The model does depend on the assumed atomic structure of the step and requires that the reconstruction exist right up to it on both sides.

We therefore used a Lorenzian function, convolved with the low-temperature line shape (that includes the resolution function and the residual steps), to fit the data of Fig. 2. The fits are good, but not perfect, showing some evidence of smearing of the effective value of $T_c$, as could be caused by strain inhomogeneities in the crystal. The results of these fits, together with the dependence of the peak height approaching the transition, are shown in Fig. 4. The height data serve to identify $T_c=1080\pm 1$ K (precision) from a fit by a power law. The exponent of $0.11\pm 0.01$ is in good agreement both with the value of $0.13\pm 0.02$ for Au(110)[2] and with the theoretical value[1] of $\frac{1}{8}$ for the appropriate symmetry classification of the ideal $1\times 2$ structure as a 2D Ising model.[18] Both the peak shift, equated with $\alpha/4$, and the peak half-width, $\beta/2+\alpha/4$, are found to diverge linearly[19] above the transition. However, the half-width diverges faster implying a nonzero value of $\beta$. From the slopes we can qualify the line-defect densities expressed in units of probability per lattice site: $\alpha=6.6t$, $\beta=2.8t$, where $t=T/T_c-1$. Apart from the unprecedented shifting, the qualitative linear broadening with $t$ is similar to that of Au(110) which corresponds to a density of antiphase domain walls $\beta=5.2t$ above the transition.[20] The linearity of the $t$ dependence of the width, as supported by the fitted correlation-length exponent, $\nu=0.95\pm 0.09$, is expected for the 2D Ising model which has $\nu=1$. Pt(110) has about the same number of defects of the same given reduced temperature, but has 2.3 times as many steps as antiphase defects. It is not clear if this ratio has any fundamental significance. Villain and Vilfan[8] predicted there might be two separate transitions, one Ising and one roughening: From Fig. 4 we can say that both kinds of defect start to appear within 5 K of the same $T_c$.

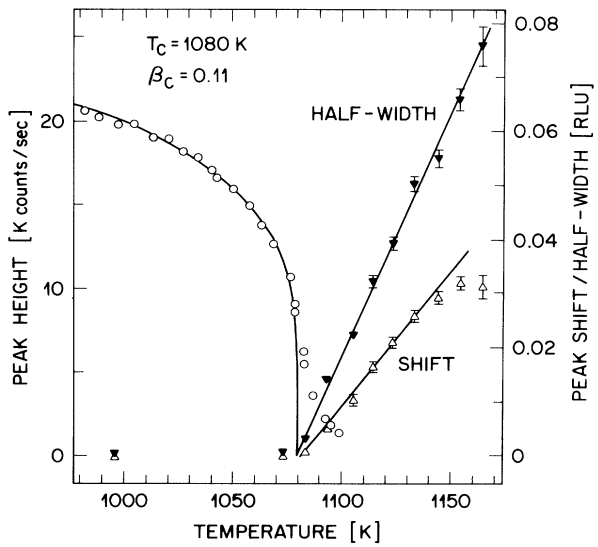


FIG. 4. Left: peak height at (1.502,0.06,0.06) vs $T$ and its fit by $(T_c-T)^{2\beta_c}$. Measurements were made both with increasing and decreasing temperature, with no signs of irreversibility. Right: variation of the fit values of half-width and shift (from 1.500 RLU) of the Lorenzian that was convolved with the $T<T_c$ profile.

The $(1\times2)$ missing-row reconstruction of Pt(110) has one unique property that makes the simple interpretation of these experiments possible: A unit-height step dividing two regions of ordered reconstructed surface introduces a quadrature phase difference which leads to shifted half-order diffraction peaks. We have shown that the peak displacement is directly proportional to the density of such steps, assuming a random distribution. This direct measure of step density and its relation to theoretical predictions is a new aspect of the study of roughening transitions; the linewidth information is much less specific since it probes the correlation length without regard for the kind of domain walls that break up the coherence. The spontaneous appearance of steps demonstrates conclusively that Pt(110) roughens above $T_c$. The simultaneous involvement of steps and reconstruction means that the ground state is at least fourfold degenerate, and so the phase transition can no longer be classed as an Ising model. Yet the critical exponents $\beta_c=0.11$ and $\nu=0.95$ are consistent with the 2D Ising model, and agree well with[2] Au(110) (although those measurements were insensitive to steps). Clearly, further theoretical work on the roughening of reconstructed surfaces is called for.

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