

The high temperature phase transition of Pt(110) (1 × 2)

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We have studied the structure and phase transition of the Pt(110)(1 × 2) surface using grazing incidence X-ray diffraction. The local structure within the (1 × 2) unit cell is of the missing row type. Along the [001] direction, i.e. perpendicular to the close packed rows, (1 × 2) terraces are separated by monatomic steps ((111) facets) as indicated by a clear and systematic shift of the superstructure diffraction peaks from the half-order positions. This peak shift is a direct measure of the step density. Like the Au(110) surface the reconstructed Pt(110) surface exhibits a continuous order-disorder phase transition at elevated temperatures ($T_c \approx 680$ K (Au) and ≈ 1080 K (Pt)). A LEED study of the Au(110) phase transition concluded that the transition could be classified as a 2D-Ising model and found the experimental critical exponents to be in good agreement. Our X-ray experiments for Pt(110), however, show that the shift of the half-order diffraction peaks changes with temperature above the transition, giving evidence that the order-disorder transition of the (1 × 2) reconstructed Pt(110) surface is a roughening transition, inconsistent with a simple 2D-Ising model.

The (110) surfaces of transition metals with face centered cubic (fcc) symmetry belong to two different classes. The first class, including the 3d elements Cu, Ni, and the 4d elements Rh, Pd and Ag, have a nonreconstructed (1 × 1) ground state for the clean surface, i.e. they keep the bulk termination. The second class of fcc metals, including the 5d elements Ir, Pt and Au, exhibits a reconstructed (1 × 2) ground state. The nature of the (1 × 2) reconstruction has been studied extensively by a number of different experimental techniques¹⁻⁹ and there is a general agreement now that the (1 × 2) phase of all three 5d metals is a missing row geometry with every second close packed [1 $\bar{1}$ 0] row missing (see top part of Figure 1).

In the case of Au(110), the missing row (1 × 2) phase has been found to be stable only in a limited temperature range. Upon heating, the half-order superlattice LEED-spot was seen to change shape with temperature and eventually disappeared at a critical temperature $T_c \approx 0.49T_M \approx 650$ K (with T_M being the melting temperature), indicating a continuous phase transition from an ordered (1 × 2) state into a disordered (1 × 1) phase¹⁰. Campuzano *et al*¹⁰ have analysed this phase transition in terms of a two dimensional order-disorder transition and determined critical exponents consistent with the predictions of the 2D-Ising model, which, due to the p2mm symmetry of the Au(110)(1 × 2) surface, is indeed the appropriate universality class¹¹.

A considerable amount of disorder, however, has also been observed to be present in the low temperature missing row phase of all three metals Ir, Pt and Au¹⁻⁹. While the coherence along the [1 $\bar{1}$ 0] direction (parallel to the close packed rows) extends over several hundred Å, the coherence length along the [001] direction (perpendicular to the rows) hardly surpassed 100-200 Å. Scanning tunneling microscopy⁷ assigned this intrinsic disorder to the presence of some (1 × 3) and (1 × 4) reconstructed regions, which are induced by a micro (111)

faceting. In theoretical studies it has been shown that the (1 × 2) missing row configuration is indeed only marginally stable with respect to the 'higher' missing row states (1 × 3, 1 × 4, ..., 1 × n). The energy difference between any of the (1 × n) phases of Au(110) has been calculated to be less than 10 meV per atom¹². Based on this ground it has been argued by several authors that the missing row configuration should be thermally unstable with respect to the formation of (111) microfacets, giving rise to a 'rough' surface at elevated temperatures. While Villain and Vilfan¹³ have predicted a succession of two transitions, an Ising-like order-disorder transition at $\sim 0.50T_M$ (spontaneous proliferation of antiphase Ising-defects, Figures 1(c, d) followed by a roughening transition at $\sim 0.57T_M$ (onset of (111) micro faceting generating single height steps, Figures 1(e, f), Levi and Touzani¹⁴ have found no evidence for an Ising-like transition but predicted a direct roughening transition. The roughening transition of non-close-packed surfaces is currently of great interest^{15,16}. Above the roughening temperature the height correlation function is expected to diverge logarithmically and give rise to a power-law lineshape, observed for example recently on Ag(110)¹⁷.

Here we report on X-ray diffraction studies of the thermal behaviour of the Pt(110)(1 × 2) surface. Measurements were made in the vacuum system described in detail in ref 18 using the 4-circle diffractometer at beamline X16A of the National Synchrotron Light Source. The longitudinal resolution of the diffractometer was set to 0.02 Å⁻¹ FWHM. The Pt crystal has been oriented *ex situ* to about 0.1° of the (110) orientation and polished before mounting to the sample holder. The sample temperature could be varied between 300 and 1600 K and was measured by a chromel-alumel thermocouple spot welded to the crystal. The surface was cleaned by argon ion bombardment and subsequent annealing in an oxygen atmosphere in the usual way¹⁹ until no contamination could be detected by Auger spectroscopy. The structure of the reconstructed Pt(110) surface was derived by analysis of relative Bragg peak intensities²⁰. At

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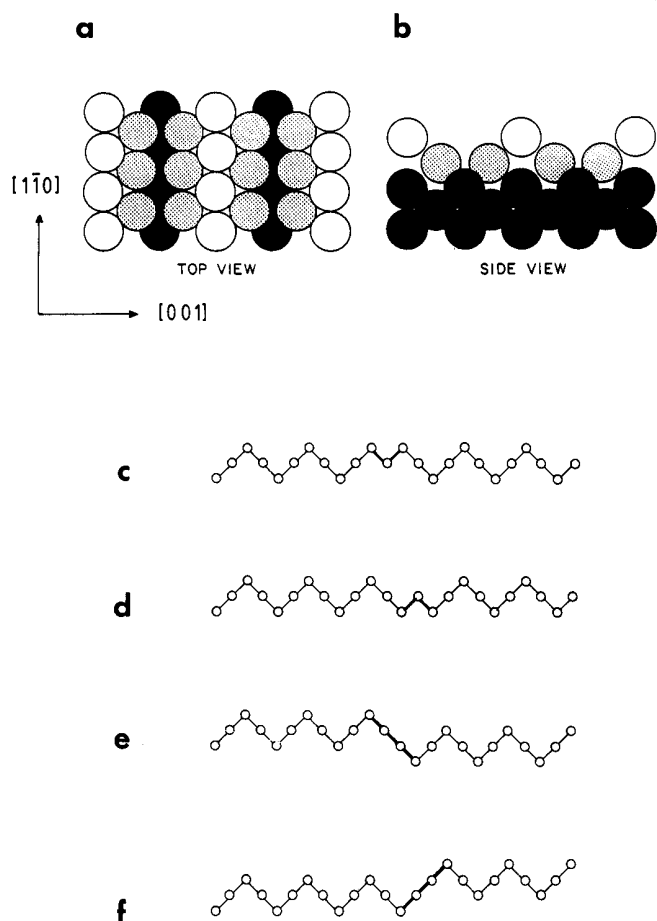


Figure 1. Geometry and thermal excitations of the fcc(110)(1 × 2) missing row reconstructed surfaces. (a) Top view, and (b) side view of the missing row geometry. (c-f) Thermal excitations of this surface; (c, d) Ising-like antiphase defects, and (e, f) monatomic steps, i.e. (111) micro facets.

low temperatures the surface has a (1 × 2) missing row structure, in which every second row of atoms in the surface layer is absent (see Figure 1). A substantial contraction of the first interlayer spacing and a modest lateral intralayer pairing in the second layer have been inferred.

So far the only experimental hint of a high temperature phase transition at the Pt(110) surface is a slight core level shift seen in photoemission at 940 ± 50 K analogous to the same effect in Au(110) at 620 K²¹. The diffraction data presented here clearly establish this phase transition, as is apparent by inspection of Figure 2 displaying the half-order diffraction peak height in the temperature interval 1000–1100 K. The critical temperature, defined as the inflection point in the curve, is found to be $T_c = 0.53T_M = 1080 \pm 50$ K. In many ways we find similar behaviour to Au(110), the peak height data of which are also included in Figure 2, with one important difference: above T_c monatomic steps are created spontaneously and their density diverges with temperature consistent with a roughening transition but inconsistent with a simple two dimensional Ising-like transition.

The experimentally observed half-order diffraction peaks have two characteristics: they are broad in the [001] direction but sharp in the orthogonal [110] direction and always displaced

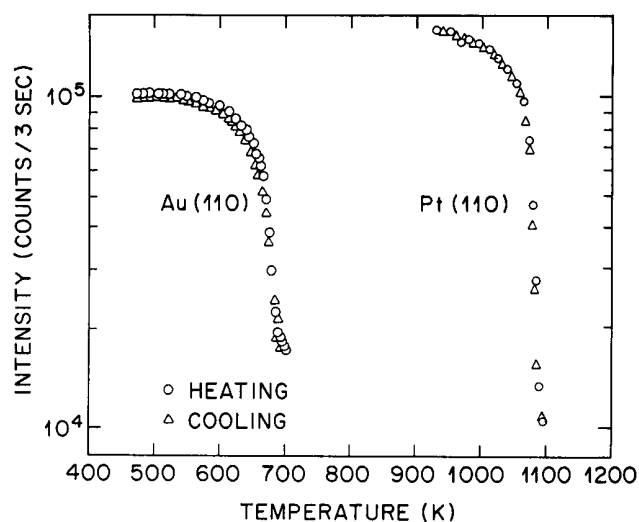


Figure 2. Peak height of the half-order spot (1.502, 0.06, 0.06) vs T for the (110)(1 × 2) surfaces of Pt and Au.

slightly from the exact half order position along [001]. A freshly sputtered sample annealed at 775 K for about one hour generates a rather broad diffraction peak with the center significantly shifted by about 0.03 reciprocal lattice units (RLU) to higher wave vectors. Only a further careful anneal at 990 K for several hours eventually sharpens the line and brings the peak center very close to the half-order position. In the inset of Figure 3 a longitudinal diffraction scan characteristic for such a carefully annealed surface is shown; the wave vector shift now is less than 0.001 RLU. The uniaxial broadening and shift implies disorder in one direction only, i.e. must be associated with line defect oriented perpendicular to the [001] direction. An identical pattern of uniaxially shifted and broadened half order diffraction peaks was observed earlier by Robinson *et al*²² for the Au(110) surface and can be explained conclusively in terms of randomly distributed single height steps on the surface (i.e. excitations of the type (e, f) in Figure 1). It was further demonstrated that the peak shift of the half-order spots is exclusively related to the density of these monatomic steps^{22,23}, while Ising-like defects (excitations (c, d) in Figure 1) would only result in a symmetric peak broadening. Indeed, (111) micro facets are also the predominant defects seen in scanning tunneling microscope images of Au(110) and Pt(110)^{7,24}.

The basic result of this study is that the half-order diffraction spots not only gradually disappear with rising temperature but also show a peak shift which is temperature dependent as demonstrated in Figure 3. After careful annealing, the crystal gave the lineshape shown in the inset of Figure 3. Also 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 is apparent, in view of the direct link between step density and shift^{22,23}, 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 diffraction peak profiles in Figure 3 quantitatively we have constructed a general model of surface disorder for the fcc(110)(1 × 2) surfaces that contain both randomly distributed monatomic steps (excitations (e, f) in Figure 1)

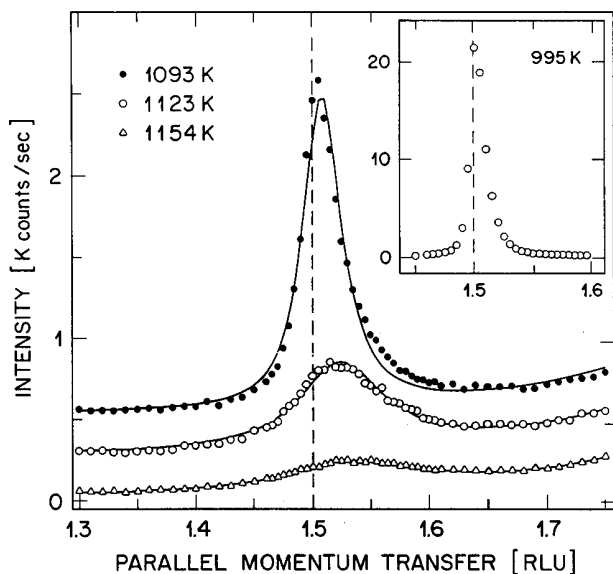


Figure 3. Temperature dependence of the half-order diffraction peak lineshape ($h, 0.06, 0.06$) obtained by scanning h . Thermal expansion of the crystal has been corrected by adjustment of the lattice parameter values. Inset is the $T < T_c$ lineshape. The shift of the peak to larger h as the line broadens with $T > T_c$ is clearly apparent.

and antiphase Ising-defects (excitations (c, d) in Figure 1) discussed in detail in ref 25. In this model, the peak shift is solely correlated with the step density while the peak width scales with the density of steps and of Ising-defects. A detailed analysis of the diffraction profiles in the phase transition region reveals a linearly diverging peak shift and width above T_c . However, the half width diverges faster implying a nonzero density of Ising-defects. From the slopes we can quantify the line defect density in units of probability per lattice site for the monatomic steps $\alpha = 0.0061(T - T_c)$ and for the Ising-defects $\beta = 0.0026(T - T_c)$.

In conclusion, we have examined the high temperature phase transition of the Pt(110)(1 × 2) surface. We observe only one

single transition at 1080 K which is predominantly a roughening transition but also involves the creation of antiphase Ising-like defects. We note that the LEED study of the Au(110) phase transition¹⁰ was indeed insensitive to proliferation of steps because the diffraction profiles were measured at a perpendicular momentum transfer of about 0.5 reciprocal lattice units, where the step induced shift of the half order Bragg peaks vanishes.

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