# Orientational Epitaxy of the Hexagonally Reconstructed Pt(001) Surface

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We describe x-ray-scattering studies of the orientational epitaxy displayed by the hexagonally reconstructed Pt(001) surface. At 1685 K, the reconstructed surface layer undergoes a continuous rotational transformation with respect to the underlying bulk and exhibits mean-field behavior. A second, discontinuous rotational transformation is observed at 1580 K. These results are inconsistent with the predictions of current theories and lead us to propose a mean-field description of rotational transformations.

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An important aspect of the growth of one crystal upon another involves their relative orientation: How are the high-symmetry directions of the ad-lattice and of the substrate lattice aligned? Our present understanding of this question has been guided by the calculations of Novaco and McTague [1], who explicitly considered incommensurate monolayers of rare gases adsorbed on a rigid, basal plane substrate of graphite. They showed that, even though there is no translational registry at the interface, there may exist a preferred orientation. This is called orientational epitaxy. Their calculations further revealed that the high-symmetry directions of an incommensurate overlayer may be rotated away from the high-symmetry directions of the substrate and that the rotation angle is determined by the incommensurability of the overlayer and by its phonon dispersion relations. In many instances, most notably for the rare gases on graphite [2] and for alkali metals on transition-metal surfaces [3], the predictions of Novaco and McTague describe the orientational epitaxy of an adsorbed layer. Other systems for which the rotational epitaxy has been characterized include layers of alkali metals intercalated into graphite [4], *in situ* deposited monolayers of Pb on Ag(111) and Au(111) electrodes [5], crystallites of Pb deposited on Si(111) and Ge(111) substrates [6], and clean Au(001) surfaces held in vacuum [7] and under electrochemical conditions [8].

In this paper, we describe the rotational behavior exhibited by the clean (001) surface of Pt between 300 and 1820 K. We have found that between $T=1685$ and 1820 K, the surface reconstructs to form a buckled, hexagonal monolayer [9] on top of the bulk planes of square symmetry lying immediately beneath. The top layer is incommensurate in both directions within the surface plane, and the average area per atom is contracted by 8% relative to its value in a bulk (111) plane. In this phase, a hexagonal high-symmetry direction is aligned with the cubic (1,1,0) direction. However, as the temperature is reduced below $T_c=1685$ K, there is a structural transformation in which domains of the hexagonal overlayer rotate continuously to angles $\pm 0.9°$ away from the bulk (1,1,0) direction. Remarkably, the rotational transformation exhibits mean-field behavior: That is, the dependence of the rotation angle on temperature follows a one-half power law versus reduced temperature $\varepsilon=(T_c-T)/T_c$. At 1580 K, there is a second, discontinuous transformation, leading to coexistence among domains of slightly different rotation angle. Throughout the aligned and rotated hexagonal phases, the incommensurability varies only weakly, but in such a way that the area per atom remains approximately constant.

The mean-field behavior exhibited near $T_c$, the observed relationship between the rotation angle and incommensurability, and the coexistence of domains with differing rotation angles all stand outside a simple application of the theory of Novaco and McTague [1] to Pt(001). These results motivate renewed theoretical consideration of orientational epitaxy, especially for metals. In this latter regard, we show that the phase behavior of Pt(001) is strikingly similar to that of Au(001), when both are considered on a temperature scale normalized by the bulk melting temperature $T_m$ [7,10]. In addition, we have developed a mean-field theory, which qualitatively describes some aspects of the rotational behavior observed for both Pt(001) and Au(001) surfaces. A detailed account is given in Ref. [10].

X-ray-diffraction experiments were performed on beam line X22C at the National Synchrotron Light Source using a UHV apparatus equipped with standard surface diagnostics. The Pt sample, an (0,0,1)-oriented disk with mosaic 0.01° full width at half maximum (FWHM), was heated by electron-bombardment techniques. Its temperature was monitored with a $\mathrm{WRe}_{0.05}$-$\mathrm{WRe}_{0.26}$ thermocouple and by direct measurement of the Pt lattice constant. High-resolution experiments were performed in a glancing incidence geometry at a fixed surface normal index $L=0.07$ [7,10]. The radial resolution (FWHM), obtained at a momentum transfer of $\sim 2$ Å$^{-1}$, was 0.0011

Å$^{-1}$, for incident photons of energy 8.1 keV.

The in-plane diffraction pattern observed for Pt(001) in the aligned-hexagonal phase at 1800 K is shown in Fig. 1(a). The (1,0)*h* hexagonal reflection [7,10] lies along the (1,1,0) direction and is incommensurate with the substrate. There are, in addition, satellites of both the hexagonal and substrate reflections parallel to (1,1,0), with difference wave vector $\boldsymbol{\delta}=\boldsymbol{\tau}_1-\mathbf{G}_1$, where $\boldsymbol{\tau}_1$ and $\mathbf{G}_1$ are the wave vectors of the (1,0)*h* and (1,1,0) reflections, respectively. In the rotated-hexagonal phase [shown for 1600 K in Fig. 1(b)], all of the hexagonal reflections are split relative to the origin by the rotation angle. The principal, rotated-hexagonal reflections are (1,0)*h*+ and (1,0)*h*−, where +− indicates the sense of rotation. The corresponding splitting of the harmonics may be understood by defining the difference wave vectors $\boldsymbol{\delta}^{\pm}=\boldsymbol{\tau}_1^{\pm}-\mathbf{G}_1$. The harmonic positions are then indexed by taking the sums and differences of $\boldsymbol{\delta}^{+}$ and $\boldsymbol{\delta}^{-}$ with either a hexagonal or a substrate wave vector. These satellites originate in the buckling of the top and succeeding layers [7,10]. At 1600 K, the corrugation wave vector $\boldsymbol{\delta}^{\pm}$ makes an angle to the (1,1,0) axis of 3.8° and has a period of 13.84 Å, consistent with the results of scanning tunneling microscopy measurements [11].

A transverse scan taken through (1,0)*h* at 1768 K is shown in the top of Fig. 2. This scan was obtained by setting the x-ray momentum transfer at $\boldsymbol{\tau}_1$ and then rotating the sample about its surface normal through an angle $\theta=\pm 1.5°$. The dependence of the intensity on $\theta$, therefore, reflects the angular distribution of ordered, hexagonally reconstructed domains across the surface. In this scan, the angular width was $<0.01°$ (FWHM) with a count rate of about 40000/s. The corresponding radial peak width was $0.0014\pm0.0002$ Å$^{-1}$ (FWHM), which suggests that, at the highest temperatures, hexagonally reconstructed domains extend over distances of several thousand angstroms, and remain aligned to the (1,1,0)

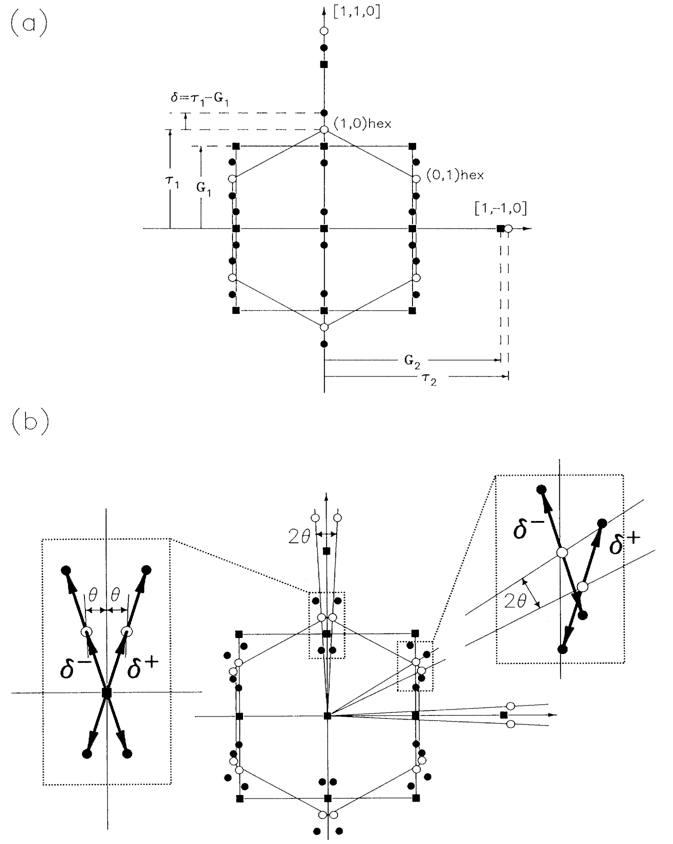

FIG. 1. Schematic in-plane diffraction pattern for Pt(001) in the (a) aligned-hexagonal and (b) rotated-hexagonal phases. Inset: Details of (1,0)*h*± and (0,1)*h*± reflections. Each symbol corresponds to a rod of scattering oriented normal to the surface. Solid squares indicate the scattering through reflections which share the symmetry of bulk (001) planes (truncation rods). Open circles indicate reflections of hexagonal symmetry. Solid circles indicate harmonics of the hexagonal and substrate reflections. The wave-vector differences $\boldsymbol{\tau}_1-\mathbf{G}_1$ and $\boldsymbol{\tau}_2-\mathbf{G}_2$ are defined along the (1,1,0) and (1,−1,0) directions, respectively.

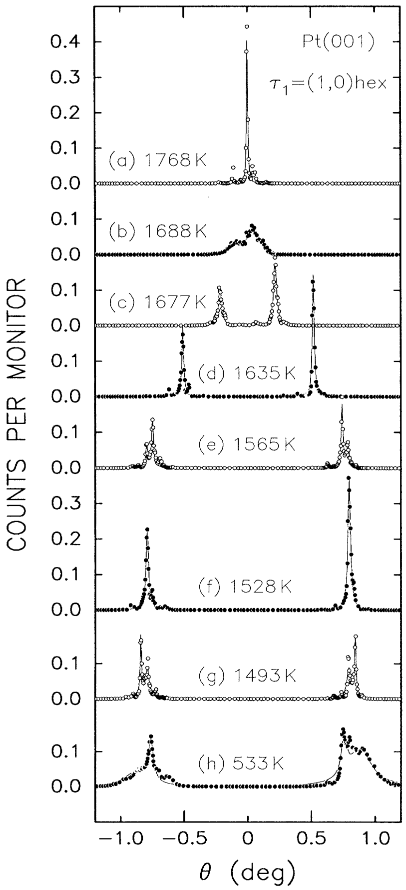

FIG. 2. Transverse scans taken through the (1,0)*h* hexagonal reflection plotted for several temperatures.

direction to within 0.01°. As the temperature is reduced below ~1685 K, the peak at (1,0)$h$ first broadens and then splits into (1,0)$h+$ and (1,0)$h-$. With decreasing temperatures, the angular separation between the peaks increases continuously. Below about 1580 K, a second pair of rotated peaks appears and remains visible for temperatures down to 300 K. This implies that rotated domains with slightly different rotation angles coexist.

The detailed temperature dependence of the rotation angle is shown in Fig. 3(a). Between $0.89T_m$ and $0.82T_m$, the rotation angle is zero. Below $0.82T_m$, it increases continuously from 0 to 0.9° (open circles), and at $0.77T_m$ a second rotation angle appears at ±0.8° (closed circles). Below $0.70T_m$, the two are approximately constant with values ±0.9° and ±0.75°. The smooth variation of the rotation angle near $T_c$ is quantified in the inset of Fig. 3(a). The solid line drawn through the data is the best fit by a power-law form $A\epsilon^{\beta}$ and gives parameters $\beta=0.47\pm0.05$, $A=2.65\pm0.4°$, and $T_c=1685\pm10$ K. Thus, the continuous rotational transformation is consistent with mean-field behavior ($\beta=\frac{1}{2}$) between $0.82T_m$ and $0.77T_m$.

The corresponding temperature dependence of the surface incommensurabilities measured along the (1,1,0) and (1,−1,0) directions is shown in Fig. 3(b). In each case, $\tau_1/G_1-1$ and $\tau_2/G_2-1$ vary smoothly by ~1% over the whole range of temperature. Specifically, $\tau_1/G_1-1$ increases for decreasing temperatures from about 0.202 to 0.204, while $\tau_2/G_2-1$ decreases from 0.0410 to 0.039. It follows that at 1800 K the hexagonal unit cell is contracted relative to an ideal Pt(111) plane by 3.9% along the (1,1,0) and (1,−1,0) directions. This leads to an average area per atom of $0.92a^2$. As the temperature is reduced, the hexagonal unit cell distorts slightly, but in such a way that the area per atom is approximately conserved.

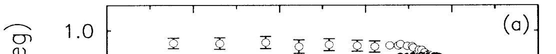

FIG. 3. (a) Rotation angle observed for hexagonally reconstructed domains of the Pt(001) surface plotted vs $T/T_m$, where $T_m=2045$ K. Inset: Variation of the rotation angle plotted vs reduced temperature $\epsilon=(T_c-T)/T_c$ on a log-log scale. (b) Incommensurabilities $\tau_1/G_1-1$, along the (1,1,0) direction (open circles), and $\tau_2/G_2-1$, along the (1,−1,0) direction (open squares), plotted vs $T/T_m$.

In the theory of Novaco and McTague [1], the strain energy induced in the incommensurate overlayer by the substrate is reduced by long-wavelength, transverse distortions. This leads to a rotation of the monolayer away from the substrate symmetry axes. In the simplest form of the theory, the rotation angle is linearly related to the incommensurability and depends on the overlayer elastic constants. For the present case, it predicts a rotation of ~7° for an incommensurability of 0.2. This deviates from any measured value by nearly a factor of 10. Moreover, while the incommensurability varies by only ~1% from $T=1800$ to 300 K, the rotation angle increases continuously from 0 to 0.9°, and a second rotation angle appears at 1580 K. This behavior cannot be accounted for straightforwardly on the basis of current theories of orientational epitaxy [1,12–14].

It seems likely that the observed discrepancies with the theory arise from several assumptions, which are adequate for describing rare gases adsorbed on a graphite surface, but invalid for Pt. These include the use of pair potentials to describe the interactions among overlayer and substrate atoms, the neglect of the overlayer and substrate buckling, and the assumption of a hexagonal monolayer adsorbed on a hexagonal substrate. For the same reasons, we believe that current theories [1,12–14] are unable to describe the orientational epitaxy observed on the hexagonally reconstructed (001) surface of Au [7,10]. In this regard, it is important to note that the phase behaviors of Pt(001) and Au(001) surfaces are strikingly similar, when considered on a temperature scale normalized by $T_m$. This is illustrated in Fig. 4, which summarizes the results of new measurements of the rotational behavior of the Au(001) surface. The observed rotation angles and normalized transformation temperatures for Au are very close to those for Pt shown in Fig. 3. The major difference between the two is that the rotational transformation in Pt(001) is mainly continuous, while in Au(001) it is strongly discontinuous.

The observed power-law dependence of the Pt rotation angle on reduced temperature near $T_c$ suggests a mean-field description of the rotational transformation. Following Nelson and Halperin [15], we have written a Hamiltonian for the orientational modes $\theta(K)$ of the overlayer

$$H=\frac{1}{2}\,\Omega\sum_{K\neq0}4\mu\theta(K)\theta(-K)+\int d^2r\left(-\frac{1}{2}\nu\theta^2+\frac{1}{4}\omega\theta^4\right), \tag{1}$$

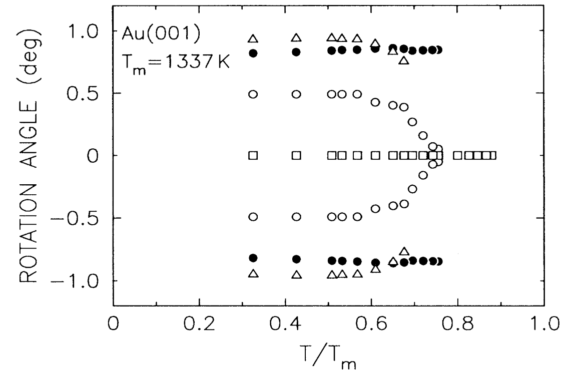

FIG. 4. Rotation angles observed for hexagonally reconstructed domains of the Au(001) surface plotted vs $T/T_m$, where $T_m = 1337$ K. Different symbols indicate differently rotated domains [10].

where $\mu$ is a Lamé coefficient, $v$ and $\omega$ are constants, $\Omega$ is the overlayer area, and $K$ is the wave vector. The first term describes the energy of transverse phonons in the overlayer and the second describes the interfacial energy as a function of the overlayer orientation. Assuming that the amplitude of each orientational mode follows a Gaussian distribution and minimizing (self-consistently) the resultant free energy with respect to the mean rotation angle $\theta_0$, we find

$$\langle \theta(K)\theta(-K)\rangle = k_B T/\Omega(4\mu + 2\omega\theta_0^2)\,. \tag{2}$$

Because $\mu$ is a constant, it follows that the mean-square orientational fluctuations have a finite amplitude for all temperatures $T < T_c$ and all wave vectors. Provided that $3\Lambda^2\omega k_B T_c/32\pi\mu^2 < 1$ ($\Lambda$ is the Debye wave vector), then

$$\theta_0 = \left[\frac{v}{\omega(1 - 3\Lambda^2\omega k_B T_c/32\pi\mu^2)}\right]^{1/2}\left[\frac{T_c - T}{T_c}\right]^{1/2}, \tag{3}$$

which is consistent with our observations in Pt(001). If, on the other hand, $3\Lambda^2\omega k_B T_c/32\pi\mu^2 > 1$, then there is a discontinuous change in rotation angle with temperature. This is reminiscent of the behavior observed in Au(001) and suggests that the mean-field theory may offer a starting point for more sophisticated calculations of orientational epitaxy in metals. There are intriguing problems outstanding: for example, to explain the occurrence in Pt of a second, discontinuous rotational transformation (leading to coexistence among domains of differing rotational angle [14]), and to clarify to what extent the closely similar band structures of Pt and Au determine their surface phase behavior.

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