Comment on "Complete Wetting on 'Strong' Substrates: Xe/Pt(111)"

In a recent Letter,[1] Kern, David, Palmer, and Comsa (KDPC) present thermal-He scattering data for Xe layers on Pt(111). They find that the incommensurate monolayer, rotated with respect to the substrate, shows a diffraction peak at small wave vector Q, that they associate to a commensurate buckling. I argue that the Q peak can be due to the static distortion of the monolayer which appears as a consequence of the rotation, and needs not be commensurate.

The substrate potential of the (111) surface of a fcc lattice is[2] $V(\mathbf{r},z)=V_0(z)+V_1(z)\sum_n \cos\mathbf{G}_n\cdot\mathbf{r}$. $V_0(z)$ has a deep minimum at a distance z_0 from the substrate; $V_1(z)$ is a positive decreasing function of z, $\mathbf{G}_n(n=1,\ldots,6)$ are the six smallest (equivalent) reciprocal lattice vectors of the substrate surface.[3] It is straightforward to include atomic displacements u_z normal to the substrate in the Novaco-McTague[4] theory of orientational epitaxy. The energy per adatom of the incommensurate monolayer is written as[5]

$$\mathcal{H}=E_0+V_0(z_0)-\mathcal{H}_\theta+\tfrac{1}{2}\sum_{\{\mathbf{q}\}}\mathcal{H}(\mathbf{q}). \qquad (1)$$

E_0 is the cohesive energy of the monolayer. $\mathcal{H}(\mathbf{q})$ are the positive energies associated to the normal modes, $\{\mathbf{q}\}$ being the vectors of the adsorbate's first Brillouin zone, and

$$\mathcal{H}_\theta=\sum_{\mathbf{Q}_n,n=1}^{6}\left[\left(\frac{V_1(z_0)}{J_L(Q_n)}\mathbf{G}_n\cdot\frac{\mathbf{Q}_n}{Q_n}\right)^2+\left(\frac{V_1(z_0)}{J_T(Q_n)}\mathbf{G}\times\frac{\mathbf{Q}_n}{Q_n}\right)^2+\left(\frac{V_1'(z_0)}{V_0''(z_0)+J_z(Q_n)}\right)^2\right]. \qquad (2)$$

The sum is over all vectors $\mathbf{Q}_n$ which satisfy $\mathbf{G}_n+\mathbf{Q}_n=\mathbf{K}$, where $\mathbf{K}$ is an adsorbate's reciprocal lattice vector. $J_L(q)=(\mathcal{K}+\mu)vq^2$, $J_T(q)=\mu vq^2$, and $J_z(q)=\frac{1}{2}(2\mu-\mathcal{K})vq^2$, where $\mathcal{K}$ is the monolayer two-dimensional bulk modulus, μ the shear modulus, and v the unit cell area. Rare gases interact via central forces, so that in the incommensurate phase, $\mathcal{K}=2\mu$, $J_z(q)=0$, and the third term in (2)—associated with buckling—plays no role in the determination of the rotation angle θ. For a misfit $m=(d^R_{\mathrm{Xe}}/d^{\sqrt{3}}_{\mathrm{Xe}})-1$, and if we assume that only the smallest $\mathbf{Q}_n$ contribute significantly to (2), $\mathcal{H}_\theta$ is maximized by

$$\theta=\cos^{-1}\left[(1+m)\frac{5+(1+m)^2}{2+4(1+m)^2}\right]\simeq\frac{m}{\sqrt{3}}. \qquad (3)$$

The modulus of the six (equivalent) $\mathbf{Q}_n$ vectors is

$$Q\cong 2K_{(12)}(m/\sqrt{3})(1+m/8)+o(m^3), \qquad (4)$$

$K_{(12)}=4\pi/d^R_{\mathrm{Xe}}$ is the modulus of the $(12)_{\mathrm{Xe}}$ reciprocal lattice vector (with KDPC's indexation). The angle ϕ between $\mathbf{Q}_n$ and the corresponding $\mathbf{K}=\mathbf{G}_n+\mathbf{Q}_n$ is given by $(|K|=K_{(12)})$

$$\sin\phi=(K_{(12)}/Q)\sin\theta\simeq\tfrac{1}{2}(1-m/8). \qquad (5)$$

For small misfits, $\phi\simeq 30°$: *the* $\mathbf{Q}_n$ *are almost in the same directions as* $\mathbf{K}_{(11)}$ *and its star.*

The minimization of (1) implies that all $\mathcal{H}(q)$ must vanish. This gives $\mathbf{u}(\mathbf{q})\simeq 0$ for all $\mathbf{q}\neq\mathbf{Q}_n$, and a static distortion of the monolayer, of wave vectors $\mathbf{Q}_n$ and amplitudes

$$u_L=[V_1(z_0)/J_L(Q)]G\cos(\theta+\phi)$$

(in plane, longitudinal),

$$u_T=[V_1(z_0)/J_T(Q)]G\sin(\theta+\phi)$$

(in plane, transverse),

$$u_z=[V_1'(z_0)/V_0''(z_0)+J_z(Q)]$$

(out of plane). Satellites at $\mathbf{Q}_n$ should therefore appear in the diffraction pattern.

In KDPC's experimental geometry the scattering plane contains $\mathbf{K}_{(11)}$; therefore it also contains the $\mathbf{Q}_n$ satellites. When we introduce their value of the misfit $m=0.096\pm0.006$ into (3), (4), and (5), the theoretical predictions are $\theta_{\mathrm{theor}}=(3.5\pm0.2)°$; $Q_{\mathrm{theor}}=0.032\pm0.002$ Å^{-1}, corresponding to a periodicity $d_{\mathrm{theor}}=4\pi/Q\sqrt{3}=22\pm2$ Å; and $\phi_{\mathrm{theor}}=(29.9\pm0.2)°$, in fair agreement with the experimental result $\theta=3.3°$, $d=23\pm2$ Å, $\phi=30°$ (uncertainty in the theoretical values is due to experimental uncertainty in m).

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