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Symmetry and rotational epitaxy of incommensurate Xe layers on Pt(111)

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High-resolution He diffraction studies of the structure and rotational epitaxy of incommensurate Xe layers on Pt(111) are reported. At completion of the commensurate $(\sqrt{3}\times\sqrt{3})R30°$ monolayer (C) a continuous phase transition to a striped incommensurate phase (SI) occurs. With increasing incommensurability the striped phase (SI) transforms at a critical misfit of $\simeq$6.5% to a hexagonal incommensurate phase (HI) in a first-order transition. Upon further increase of the misfit ($\geq$7.2%) the HI phase displays a continuous transition from an aligned to a Novaco-McTague rotated orientation (HIR). Xe on Pt(111) appears to be an ideal model system of two-dimensional phases and their mutual transitions, i.e., it is the first system showing completely the theoretically predicted sequence of C$\rightarrow$SI$\rightarrow$HI$\rightarrow$HIR transitions.

Much of the effort in surface physics is devoted to the study of two-dimensional (2D) adsorbate phases and their mutual transitions. The various phases arise as a result of competing interactions, e.g., the nearest-neighbor distance preferred by the lateral adatom interaction differs in general from the lattice periodicity which the substrate potential tries to impose. When the lateral adatom interaction dominates, the monolayer structure is incommensurate (I) with the substrate. However, if the adsorbate-substrate interaction increases the atoms of the adsorbed monolayer may occupy sites which are commensurate (C) with the substrate periodicity. By varying the conditions of coverage and/or temperature the adsorbed monolayer can undergo a commensurate-incommensurate (CI) transition.

Far from the CI transition region, as a result of the slight variation of the adsorption energy within the substrate unit cell, the incommensurate monolayer can be described as a weakly modulated solid phase. Novaco and McTague have shown that the energy of these monolayers far from commensurability is dependent on the orientation relative to the substrate and in particular that the orientation which minimizes the strain energy is expected to deviate from the main symmetry directions of the substrate.[1] The Novaco-McTague rotational epitaxy has been confirmed for various systems, including Ar (Ref. 2), Ne (Ref. 3), and Kr (Ref. 4) on graphite and Xe/Pt(111) (Ref. 5), Na/Ru(100) (Ref. 6), K/Cu(100) (Ref. 7), and K/Pt(111).[8]

On the other hand, close to the CI transition, the weakly incommensurate phase is considered as an array of commensurate domains separated by incommensurate domain walls.[9] These domains may be organized in striped or hexagonal networks. Using Landau theory, Bak, Mukamel, Villain, and Wentowska[10] emphasized the part played by the wall-crossing energy Λ. For attractive wall crossings ($\Lambda < 0$) a first-order transition from the commensurate phase to a hexagonal incommensurate phase (HI) has to be expected, while for repulsive wall crossings ($\Lambda > 0$) a second-order transition leading to parallel domain walls in a striped incommensurate phase (SI) has been predicted. At higher incommensurabilities, this striped phase (SI) is expected to transform to a hexagonal incommensurate phase by a first-order transition.[11,12] It was just recently that the symmetry-breaking CI transition into a striped phase has been observed in isotropic systems, Xe on Pt(111) (Ref. 13) and hydrogen on graphite.[14] In the case of Xe on Pt$(1\bar{1}\bar{1})$, the parallel domain walls were found to run into the $\bar{\Gamma}\bar{K}$ direction, i.e., the uniaxial compression was in the $\bar{\Gamma}\bar{M}$ direction. As predicted by theory[10,15] this $(\sqrt{3}\times\sqrt{3})R30°$-C$\rightarrow$SI transition of monolayer Xe on Pt(111) was found to be continuous, with the incommensurability close to the transition following a $\frac{1}{2}$ power law versus reduced temperature.

In this Rapid Communication I report on the behavior of the incommensurate Xe phase on Pt(111) during the transition from the striped phase to the Novaco-McTague rotated phase (HIR), when moving from small to large incommensurabilities. At a misfit of about 6.5% the SI phase transforms to a hexagonal incommensurate phase in a first-order transition. Upon further increase of the average incommensurability (misfit $\geq$7.2%) the HI phase displays a continuous transition from a $R30°$ orientation, i.e., aligned with the $\bar{\Gamma}\bar{K}$ direction of the substrate, to a Novaco-McTague rotated orientation. The maximum rotation angle of the HIR phase is $\pm3.3°$ at monolayer

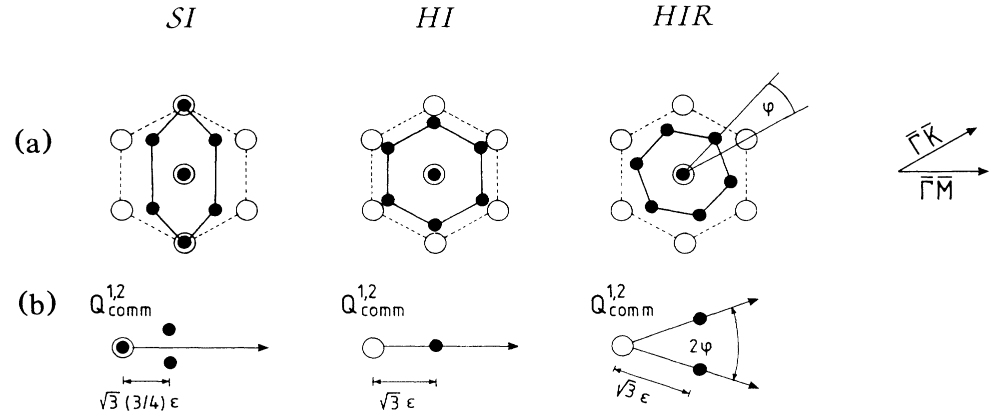

FIG. 1. (a) Real lattice and (b) schematic representation of the $(1,2)_{\rm Xe}$ diffraction features of various incommensurate Xe structures on Pt(111). SI, striped incommensurate; HI, hexagonal incommensurate; and HIR, hexagonal incommensurate rotated phase. All phases assumed to be fully relaxed. ○ denotes the $(\sqrt{3}\times\sqrt{3})R30°$ commensurate and ● the incommensurate structures. Here, the incommensurability ε is defined in the usual convention as the shift of the (1,0) diffraction peak with respect to its commensurate position.

completion (misfit 9.6%).

The experiments have been performed in an ultrahigh-vacuum high-resolution He-scattering spectrometer, described in detail elsewhere.[16] The sample was a high-quality Pt(111) surface with an average terrace width of about 3000 Å. The measurements reported here were performed with a liquid-nitrogen-cooled nozzle, generating a 18.3-meV He beam with an energy spread $\Delta E/E \simeq 1.4\%$. The He-beam generator and the detector being immobile, the total scattering angle is fixed, $\theta_i+\theta_f=90°$. Accordingly, the diffraction patterns are scanned by rotating the crystal in the scattering plane (polar scans) and about its surface normal (azimuthal scans). Both the angular divergence of the incident beam and the angle subtended by the detector opening are 0.2°.

The structure (i.e., symmetry, orientation, and lattice parameter) of the physisorbed Xe films for different coverages and temperatures has been characterized by measuring the $(2,2)_{\rm Xe}$ and $(1,2)_{\rm Xe}$ diffraction features (for definition see Ref. 5). In this Communication we will present only $(1,2)_{\rm Xe}$ spot profiles, because this diffraction order allows for a unique determination of the symmetry and orientational epitaxy of the monolayer, exemplified in Fig. 1.

Figure 2 shows 3D plots of the $(1,2)_{\rm Xe}$ diffraction order at various coverages and temperatures, illustrating the behavior of the Xe adlayer during the transition from the striped phase to the hexagonal rotated phase. The plots have been obtained by measuring series of azimuthal diffraction scans. The diffraction plot Fig. 2(a), taken from a Xe adlayer of coverage $\Theta_{\rm Xe}\simeq 0.30$ ($\Theta_{\rm Xe}=1$ corresponds to 1.5×10^{15} Xe atoms per cm^2) at a surface temperature $T_s=54$ K characterizes the striped phase of Xe with the uniaxial compression in the $\bar{\Gamma}\bar{M}$ direction. A peak at the commensurate position $Q^{1,2}_{\rm comm}=2.62$ Å^{-1} and a shallow doublet with the maximum intensity somewhere around $Q^{1,2}_{\rm comm}+0.13$ Å^{-1} is observed. From the peak position and the azimuthal splitting, as well as from the cor-

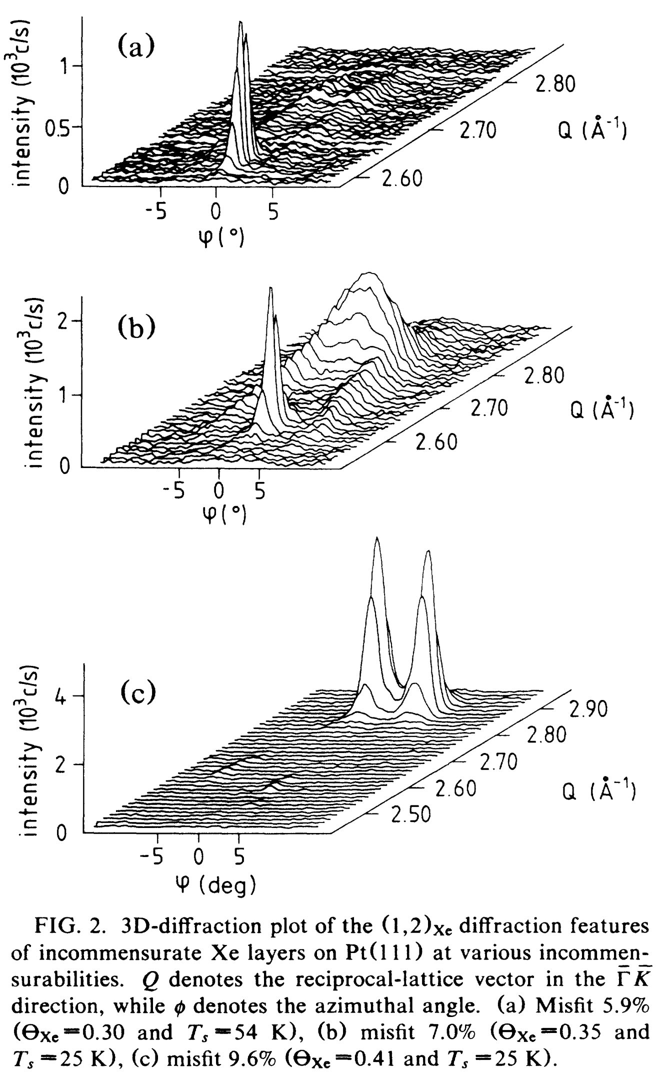

FIG. 2. 3D-diffraction plot of the $(1,2)_{\rm Xe}$ diffraction features of incommensurate Xe layers on Pt(111) at various incommensurabilities. Q denotes the reciprocal-lattice vector in the $\bar{\Gamma}\bar{K}$ direction, while ϕ denotes the azimuthal angle. (a) Misfit 5.9% ($\Theta_{\rm Xe}=0.30$ and $T_s=54$ K), (b) misfit 7.0% ($\Theta_{\rm Xe}=0.35$ and $T_s=25$ K), (c) misfit 9.6% ($\Theta_{\rm Xe}=0.41$ and $T_s=25$ K).

responding figures of the $(2,2)_{\mathrm{Xe}}$ diffraction feature,[13] an incommensurability $\varepsilon = 0.95$ Å^{-1} is deduced, corresponding to a $\overline{\Gamma M}$ uniaxial misfit $m = 5.9\%$. The weak intensity and large polar width of the doublet in Fig. 2 is due to the particular shape of the striped domains; in the $\overline{\Gamma K}$ direction parallel to the walls the correlation length is about seven times larger than in the $\overline{\Gamma M}$ direction perpendicular to the walls (for details see Ref. 13). Diffraction patterns as in Fig. 2(a), i.e., characteristic for an SI phase, have been observed in the entire misfit range $0 < m < 6.5\%$.

Plot (b) in Fig. 2 shows a slightly more compressed Xe film with average misfit $m = 7.0\%$, which has been obtained by increasing the coverage to $\Theta_{\mathrm{Xe}} = 0.35$ and cooling down the sample to 25 K. Here, three features are present: a peak at the commensurate position $Q^{1,2}_{\mathrm{comm}} = 2.62$ Å^{-1}, a weak doublet centered somewhere around $Q^{1,2}_{\mathrm{comm}} + 0.15$ Å^{-1}, and a relatively broad intense "on-axis" peak at $Q^{1,2}_{\mathrm{comm}} + 0.19$ Å^{-1}. This diffraction patterns shows that there is a phase coexistence between an SI and a nonrotated HI phase (compare with the schematic spot profiles of the various phases in Fig. 1). Diffraction patterns similar to those in Fig. 2(b), i.e., composed of a single peak at $Q^{1,2}_{\mathrm{comm}}$ and a doublet at $Q^{1,2}_{\mathrm{comm}} + (3/4)\varepsilon\sqrt{3}$ originating from an SI phase, and an on-axis peak at $Q^{1,2}_{\mathrm{comm}} + \varepsilon\sqrt{3}$ originating from a HI phase, are observed in the misfit range $6.5\% \leq m \leq 7.2\%$, in which the intensity of the $Q^{1,2}_{\mathrm{comm}} + \varepsilon\sqrt{3}$ peak progressively increases in strength with increasing misfit. Thus, we conclude that the striped incommensurate phase transforms at a critical misfit of $\sim 6.5\%$ to a hexagonal incommensurate nonrotated phase by a first-order transition.

Finally, the diffraction plot in Fig. 2(c) shows the Xe film at monolayer completion with $m = 9.6\%$ ($\Theta_{\mathrm{Xe}} = 0.41$ and $T_s = 25$ K), obviously characterizing a Novaco-McTague rotated phase with the azimuthal rotated peaks at $Q^{1,2}_{\mathrm{comm}} + \varepsilon\sqrt{3} = Q^{1,2}_{\mathrm{comm}} + 0.28$ Å^{-1}, originating from the domains which are rotated by $\pm 3.3°$ from the common orientation of the $(\sqrt{3}\times\sqrt{3})R30°$ commensurate structure (there is, of course, no "left" or "right" preference).

Figure 3 is a plot of the rotation angle ϕ as a function of the average misfit m displaying the behavior during the HI-HIR transition; the solid circles are the measured data. The dashed line is the Novaco-McTague linear response theory for a Cauchy solid (where the ratio of longitudinal c_L to transverse c_T sound velocities of the 2D monolayer is $c_L/c_T = \sqrt{3}$). Shiba[17] noted that with increasing misfit a crossover from the domain-wall regime (small incommensurabilities) to the modulation regime (large incommensurabilities) should occur, and that there should exist a critical misfit for the onset of rotation. Shiba's curve for a Cauchy solid is also drawn in Fig. 3 (dashed-dotted line); a value $l_0 = 10$ has been taken which causes the HI-HIR transition to occur at a critical misfit of 7.2%, as observed in experiment. Shiba's parameter l_0 is analogous to Frank and van der Merwe's l_0, i.e., is the distance between the domain walls in units of Xe interrow distances in the $\overline{\Gamma M}$ direction at the transition point. Shiba's theory appears to give only a qualitative account of the overall variation of rotation angle versus misfit. A quantitative agreement with the data is obtained by a power law of the form $\phi \sim (m - m_0)^{1/2}$ with $m_0 = 0.072$ (solid line in Fig. 3). A similar power-law behavior has been observed for the rotation angle of Kr layers on graphite[4] and in Cs-intercalated graphite.[18]

The observation of a finite critical misfit for the onset of rotation is also consistent with the approximate analysis of Villain[19] and the analytic treatment of Gordon and Villain.[20] They have calculated the energy associated with a small rotation of a system of parallel walls near the CI transition, and found that the domain-wall rotation should take place in the incommensurate regime (i.e., at a finite misfit) and not at the CI transition. Indeed, the Novaco-McTague model calculations[1] have been performed in the linear response approximation of the adsorbate-substrate interaction. Close to the CI transition, however, this approximation fails, and no rotation has to be expected for realistic values of the Lamé coefficients of the adlayer. Experimentally, finite critical misfits for rotational onset have also been observed for Kr on graphite[4] and CF_4 on graphite.[20]

In Shiba's theory, the rotational transition takes place at the crossover from the domain-wall regime to the modulation regime. How does this prediction agree with experiment? In the case of Kr on graphite it seems to be appropriate. Indeed, the observed critical misfit for the onset of rotation $\simeq 3.5\%$ goes along with the transition from the domain wall to the modulation regime.[4] In the case of Xe on Pt(111), however, the situation is different. The critical misfit for the onset of rotation is $\simeq 7.2\%$; a misfit, already located in the region where the adlayer topology is fully consistent with the description as a weakly modulated solid phase. Indeed, detailed studies of the C-SI transition of Xe on Pt(111) (Ref. 13) have shown that the description of the SI phase in terms of domain-wall networks is only justified for misfits less than $\simeq 3\%$. For larger incommensurabilities the striped phase is in fact an uniaxial compressed phase, i.e., a *strongly relaxed* "domain-wall" phase with the wall width of the same

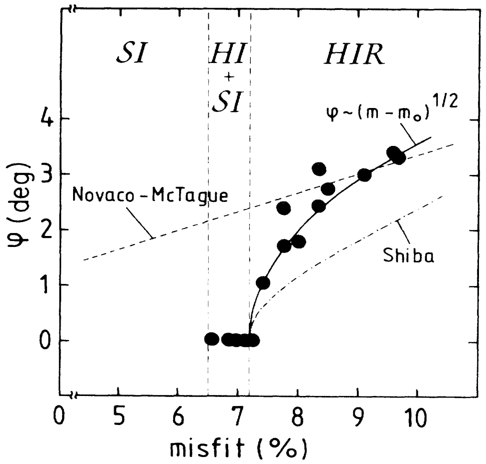

FIG. 3. Rotation angle ϕ of Xe on Pt(111) vs misfit m. The dashed line is the Novaco-McTague prediction, and the dashed-dotted line is Shibas prediction, both for a Cauchy solid, whereas the solid curve is a power-law fit of the form $(m - m_0)^{1/2}$ (see text).

magnitude as the wall distance. Anyway, the extended misfit range in which the striped phase of Xe is stable raises a problem. Shiba expected the striped phase to be stable only in a very narrow range near the CI transition; a result which was confirmed recently in calculations of Halpin-Healy and Kardar.[12]

The existence of the various solid Xe phases (C, SI, HI, and HIR) on such a "smooth" surface like the hexagonal close-packed (111) face of platinum seems to be surprising in itself. As already noted in the beginning, the various solid phases of physisorbed adlayers arise as a result of competing interactions; lateral adatom versus adsorbate-substrate interactions. For a long time, the variation of the adsorption energy of noble gases within the substrate unit cell of close-packed metal surfaces (hollow, bridge, or on-top site) has been assumed to be negligible, and consequently the occurrence of the various adlayer phases on these substrates has been expected to be quite unlikely. A theoretical study of the Xe/Pt(111) system by means of molecular-dynamics techniques has been published very recently.[21] The lateral corrugation of the holding potential used in Black and Bopp's calculation (28 K hollow bridge site and 168 K hollow on-top site) was so small, that even the existence of the commensurate $\sqrt{3}$ structure, which was found in experiment to be stable in an extended coverage ($\Theta_{\mathrm{Xe}}=0-0.33$) and temperature ($T_s=62-99$ K) range,[5] was not reproducible in the molecular-dynamics calculations. This corrugation (the hollow bridge) has been measured directly for Xe on W(110)[22]—a rather close-packed surface—and estimated from thermodynamic and mobility measurements for Xe on Pt(111).[23] The obtained values of 545 and 350 K, respectively, are about one order of magnitude larger than the values used in the molecular-dynamics calculations.[21] In view of these experimental corrugation values the occurrence of rich and subtle two-dimensional phase transitions in the Xe/Pt(111) system has in fact to be expected. New molecular-dynamics calculations of the Xe/Pt(111) system taking into account this substantial diffusional barrier would be desirable in order to gain more insight in the microscopic mechanisms of the C-SI-HI-HIR transitions.

Finally, we note that the rotational epitaxy of Xe on Pt(111) is very sensitive to the quality of the substrate surface (see also Ref. 24). When using weakly sputtered surfaces (defect densities 1–5% instead of $<0.1\%$) or with CO- or H-contaminated surfaces, the Novaco-McTague rotation of incommensurate Xe layers is inhibited.

In summary, the following picture of the incommensurate phase of monolayer Xe physisorbed on Pt(111) appeared. At completion, or by cooling below 62 K, of the $(\sqrt{3}\times\sqrt{3})R30°$ commensurate phase, a continuous phase transition to a striped incommensurate phase with the uniaxial compression in the $\bar{\Gamma}\bar{M}$ direction occurs. The SI phase is stable in the entire misfit range $0<m<6.5\%$. At a critical misfit of $\sim 6.5\%$ the striped phase transforms to a hexagonal incommensurate $R30°$ phase (HI) by a first-order transition. Upon further compression the HI phase displays a continuous transition from the $R30°$ orientation to a rotated orientation (HIR). The onset of rotation occurs at a critical misfit of 7.2% and the rotation angle follows a power-law form with the mean field exponent $\beta=\frac{1}{2}$. Thus, Xe on Pt(111) appears to be the first 2D system displaying the full sequence of $\mathrm{C}\rightarrow\mathrm{SI}\rightarrow\mathrm{HI}\rightarrow\mathrm{HIR}$ transitions with increasing incommensurability.

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[1] A. D. Novaco and J. P. McTague, Phys. Rev. Lett. **38**, 1286 (1977).

[2] C. G. Shaw, S. C. Fain, and M. D. Chinn, Phys. Rev. Lett. **41**, 955 (1978).

[3] S. Calisti and J. Suzanne, Surf. Sci. **105**, L255 (1981).

[4] K. L. D'Amico, D. E. Moncton, E. D. Specht, R. J. Birgeneau, S. E. Nagler, and P. M. Horn, Phys. Rev. Lett. **53**, 2250 (1984).

[5] K. Kern, R. David, R. L. Palmer, and G. Comsa, Phys. Rev. Lett. **56**, 620 (1986).

[6] D. L. Doering and S. Semancik, Phys. Rev. Lett. **53**, 66 (1984).

[7] T. Aruga, H. Tochihara, and Y. Murata, Phys. Rev. Lett. **52**, 1794 (1984).

[8] G. Pirug (private communication).

[9] J. A. Venables and P. S. Schabes-Retchkiman, J. Phys. (Paris) Colloq. **38**, C4-105 (1977).

[10] P. Bak, D. Mukamel, J. Villain, and K. Wentowska, Phys. Rev. B **19**, 1610 (1979).

[11] S. N. Coppersmith, D. S. Fisher, B. I. Halperin, P. A. Lee, and W. F. Brinkman, Phys. Rev. B **25**, 349 (1982).

[12] T. Halpin-Healy and M. Kardar, Phys. Rev. B **31**, 1664 (1985).

[13] K. Kern, R. David, P. Zeppenfeld, R. L. Palmer, and G. Comsa, Solid State Commun. **62**, 391 (1987).

[14] S. Fain and H. Wiechert (private communication).

[15] V. L. Pokrovsky and A. L. Talapov, Phys. Rev. Lett. **42**, 65 (1979).

[16] R. David, K. Kern, P. Zeppenfeld, and G. Comsa, Rev. Sci. Instrum. **57**, 2771 (1986).

[17] H. Shiba, J. Phys. Soc. Jpn. **48**, 211 (1980).

[18] R. Clark, N. Caswell, S. A. Solin, and P. M. Horn, Phys. Rev. Lett. **43**, 2018 (1979).

[19] J. Villain, Phys. Rev. Lett. **41**, 36 (1978).

[20] M. B. Gordon and J. Villain, J. Phys. C **15**, 1817 (1982).

[21] J. Black and P. Bopp, Phys. Rev. B **34**, 7410 (1986).

[22] J. R. Chen and R. Gomer, Surf. Sci. **94**, 456 (1980).

[23] K. Kern, P. Zeppenfeld, R. David, and G. Comsa (unpublished).

[24] K. Kern, P. Zeppenfeld, R. David, and G. Comsa, Phys. Rev. Lett. **57**, 3187 (1986).