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# The Novaco-McTague Rotated Xe Monolayer on Pt(111): A High-Order Commensurate Locked Phase

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**Abstract.** The structural analysis of the physisorption system Xe/Pt(111) by means of high-resolution helium diffraction shows that the Xe monolayer exhibits a variety of structural phases: commensurate, incommensurate and "incommensurate" rotated. The observed buckling of the rotated phase demonstrates that a fraction of the Xe atoms is locked in high symmetry sites in agreement with the theoretical "coincident site lattice" concept of Fuselier et al., i.e. the rotated phase is a higher-order commensurate phase.

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Physically adsorbed monolayers on crystal surfaces provide experimental realization of two-dimensional (2D) model systems of condensed matter, and, as such, are receiving much interest [1]. This communication focusses on the structure of the 2D-solid phases of Xe adsorbed on a nearly defect free Pt(111) surface up to monolayer completion. A particular emphasis is put on the "incommensurate" rotated Xe phase, as observed at monolayer completion. The method of investigation is high-resolution helium diffraction. Besides its high sensitivity and good momentum resolution, He diffraction is characterized by two outstanding features: nondestructiveness and independence on the nature of the substrate. The experimental details have been discussed elsewhere [2]; here only the properties relevant to the present experiment are given. The total scattering angle is fixed; i.e. $\vartheta_i + \vartheta_f = 90°$. A He beam with an energy of 17.1 meV and a monochromaticity of $\Delta\lambda/\lambda \simeq 0.6\%$ is used. Both, the angular spread of the incident beam and the angle subtended by the ionizer opening are equal to 0.2°. The sample is a high quality Pt(111) surface with a defect density less than 0.1% [3].

The structural analysis of the system Xe/Pt(111) by means of this technique shows that the Xe monolayer exhibits a variety of structural phases [4]: commensurate, incommensurate, and "incommensurate" rotated. The corresponding schematic phase diagram is shown in Fig. 1. For coverages $\theta < 0.33$ ($\theta = 1$ corresponds to $1.5 \times 10^{15}$ Xe-atoms per cm$^2$) and for surface temperatures 61 K $< T <$ 99 K a $(\sqrt{3} \times \sqrt{3})$R30° commensurate phase (C) exists. The lattice constant and average domain size in this phase as determined from diffraction peak positions and widths are $4.80 \pm 0.02$ Å and $\sim 800$ Å, respectively. The phase denoted by I in Fig. 1 is, like the C phase, rotated by 30° with respect to the substrate, but has a lattice vector apparently incommensurate with low-order lattice vectors of the substrate. The size of the lattice vectors varies with $T$ and $\theta$. The average domain size of this phase is about 150 Å. The I-phase exists for $\theta < 0.33$ ($T < 55$ K) and $0.33 < \theta < 0.38$ ($T < 99$ K). The phase denoted by $R$ consists of domains rotated from the common orientation of the C and I phases. The "incommensurate" rotated phase exists for $\theta > 0.38$ and its average domain size is $\sim 300$ Å. At monolayer completion ($\theta = 0.41$), the maximum rotation angle with respect to the C and I phases is $\pm 3.3°$ at a lattice constant of $d_{Xe} = 4.33 \pm 0.03$ Å.

The numbers above which characterize the "incommensurate" rotated Xe layer at monolayer completion are obtained from the diffraction patterns in Fig. 2. The patterns represent the polar and azimuthal (inset) He intensity scans vs. polar angle $\vartheta_f$ and

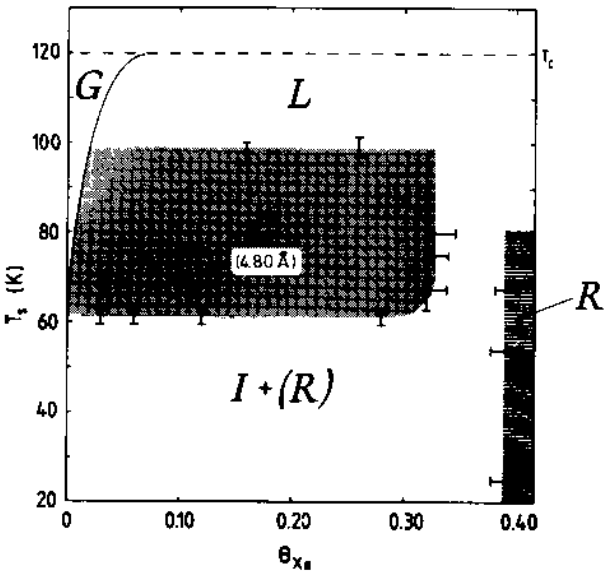


Fig. 1. Phase diagram of Xe on Pt(111). C, I, and R denote the commensurate $(\sqrt{3}\times\sqrt{3})$R30°, the incommensurate and the incommensurate rotated 2D-solid phases, respectively; G and L denote the 2D-gas and 2D-liquid, respectively

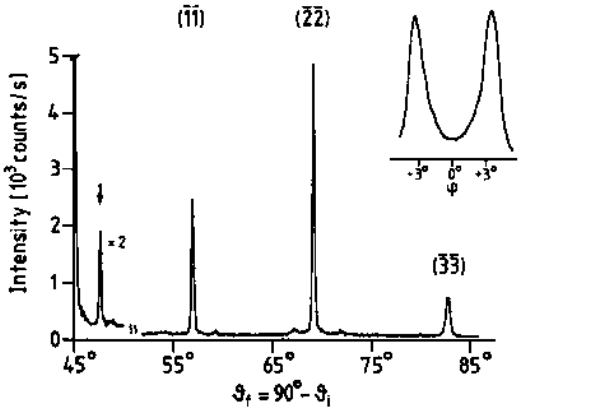


Fig. 2. Polar and azimuthal (inset) He-diffraction patterns of a rotated Xe monolayer; He beam energy 17.1 meV; surface temperature $T = 25$ K (see text)

azimuthal angle $\phi$ taken from such a layer at $T = 25$ K. The Xe is adsorbed from the gas phase at a Xe pressure of about $7\times10^{-8}$ mbar. The Xe layer is carefully annealed at $T < 50$ K and then cooled down to the monitoring temperature. The completion of the Xe monolayer is ascertained within a few percent by means of a novel procedure which takes advantage of the substantial difference between the frequency of first and second Xe-layer phonons; the procedure is described elsewhere [2]. The polar scan in Fig. 2 is taken in the $[11\bar{2}]$ orientation of the Xe domains rotated $\phi = -3.3°$ (see inset), i.e. of the R26.7° domains. The azimuthal scan of the $(\bar{2}, \bar{2})$-diffraction peak shown in the inset demonstrates that the number of domains rotated $\phi = \pm 3.3°$ are approximately equal.

The occurrence of the rotation of adlayers has been theoretically predicted by Novaco and McTague [5]. They have shown that the energy of a monolayer is dependent on its 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. The calculations emphasize the interconversion of the transverse and longitudinal energy strains, as discussed in detail by several authors [5–7]. As a result, a simple expression relating the misfit (between adlayer and substrate lattice constants) and the adlayer rotation angle is obtained. This expression has been fairly well confirmed experimentally for rare gases on graphite and also by the values obtained in the present experiment for Xe/Pt(111). Fuselier et al. [8] have extended this analysis and introduced an intuitive new concept: the "coincident site lattice". They point out that energetically favorable monolayer orientations are obtained for structures which have a higher-order commensurability (every $p$-th adatom is located in high symmetry sites). Obviously, the larger the fraction of adatoms located in high symmetry sites (i.e., the lower $p$), the larger the energy gain and the better the rotated layer is locked. This "coincident lattice" concept of Fuselier et al. which transforms the "incommensurate" rotated layers in higher order commensurate ones is very appealing. In spite of this, it remained so far almost unnoticed. This is probably because a truly incommensurate layer can be hardly distinguished from a higher-order commensurate one simply comparing the lattice constant values of the adlayer and the substrate, the only pertinent figures supplied in the experiments done so far. In particular, for misfits of say 10% or lower and for $p$ values larger than say five, the experimental error in measuring lattice constants would not allow to make a reliable distinction. Also in this case, He scattering is able to resolve the issue. Indeed, the sharp feature located near the specular beam marked by an arrow in Fig. 2 appears to be the proof that the rotated Xe layer is high-order commensurate with $p = 11$, i.e. with each elevenths Xe atom located in a high-symmetry position. The position of this peak corresponds to a superstructure with a period of $23 \pm 2$ Å. This can be assigned to a buckling of the Xe layer, due to the presence of a certain fraction of Xe atoms in high symmetry sites, probably in three-fold hollow ones. These atoms are located somewhat deeper than the other Xe atoms leading to a periodic buckling of the monolayer. The higher-order commensurability is thus directly accessible to a He-diffraction experiment.

Let us examine the situation in some more detail. The $23 \pm 2$ Å period is compatible with $5 \times d_{R-Xe} = (21.70 \pm 0.15)$ Å. We assume that the domain rotates around one Xe atom in a three-fold hollow site and that the Xe atoms have a definite preference for either fcc or hcp sites. Before rotation, e.g. in the $(\sqrt{3} \times \sqrt{3})R30°$ structure, the six Xe atoms located five lattice constants away on the three symmetry axes around the rotation center are at a distance $5 \times d_{C-Xe} = 24.0$ Å from the center. When the coverage is increased (i.e., the Xe lattice constant decreased) and the domain starts to rotate, the Xe atoms leave their sites. For each of the six Xe atoms considered, the nearest site of the same type and resulting in a smaller lattice constant is located at 21.64 Å $= 5 \times 4.33$ Å from the center and corresponds to a domain rotation of 3.67°. The distance is in agreement with the experimental value, while the rotation is 10% off. A better agreement is obtained by assuming that the six Xe atoms eleven lattice constants from the center determine the locking of the layer. The corresponding lattice constant and rotation angle are 4.37 Å $= 48.08/11$ Å and 3.30°, respectively, both in agreement with the experiment. The actual buckling period is not 48.08 Å but 24.04 Å [also in good agreement with the experimental value $(23 \pm 2)$ Å] because the fifth and the sixth Xe atoms are less than 0.25 Å from a preferred three fold hollow site and thus located nearly as "deep" as the central and the elevenths Xe atom.

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