

Incommensurate to High-Order Commensurate Phase Transition of Kr on Pt(111)

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We propose and demonstrate here a criterion, based on thermal expansion, which discriminates unambiguously between "floating" and "locked" layers. The first observation of a phase transition between an incommensurate "floating" and a high-order commensurate "locked" phase in two dimensions is reported. High-resolution He-diffraction results show a first-order transition in Kr layers on Pt(111) at coverages of ~ 0.8 monolayer with a lattice-parameter jump of ~ 0.1 Å. In the "locked" phase every sixth Kr atom is located at a preferred adsorption site (threefold hollow) forming a hexagonal $(5 \times 5)R0^\circ$ superstructure.

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The claim of this Letter—the observation of a first-order phase transition between an incommensurate "floating" and a high-order commensurate "locked" phase—has the trivial implication that the two phases are experimentally distinguishable. Bak¹ defines the incommensurate phases as opposed to higher-order commensurate ones: "In two dimensions the incommensurate phase (at $T \neq 0$) is a 'floating' phase without complete long-range order and *it does not 'lock-in' at high-order commensurate phases*" (Ref. 1, p. 587); but he states further that "Experimentally it is impossible to distinguish between a high-order C structure and an incommensurate structure" (Ref. 1, p. 590). This is a challenge for the experimentalist. If this statement is true, our claim is meaningless.

The statement is certainly true, if the only experimental information considered is the ratio of the overlayer and substrate lattice parameters. Indeed, one can always find one rational fraction (in fact an infinity) lying within the confidence range of the experimental value of the lattice-parameter ratio; i.e., the lattice-parameter ratio supplied by the most refined experiment is always compatible with a high- (enough) order commensurate phase. There are, however, other experimentally accessible parameters which make possible a distinction between an incommensurate floating and a locked layer. In a recent paper² we have tried to take advantage of the fact that the locking of a high-order commensurate adlayer is due to a fraction of the adlayer atoms being located at high-symmetry, high-bonding substrate sites. These locked atoms differ in general from the nonlocked ones by being located deeper (or less deep) on the substrate surface. This results in a periodic adlayer buckling of the type we have been able to observe as a superstructure in the thermal-He-diffraction pattern taken from a full Xe monolayer on Pt(111).² However, this kind of argumentation seems to be weakened by a very recent Comment due to Gordon.³ She is right in arguing that the superstructure we had observed could be due "to the static distortion of the monolayer, which appears as a consequence of the [Novaco-McTague] rotation, and

[thus the buckling] needs not be commensurate." Accordingly, from the mere existence of the adlayer buckling one should not conclude that the adlayer is high-order commensurate.

We propose and use here another experimental criterion, which we feel is able to distinguish unequivocally between a floating and a locked rare-gas monolayer: the thermal expansion. Indeed, a floating layer is expected to expand thermally very much like the 3D body consisting of layer atoms, while a locked layer has to follow by definition the expansion of the substrate to which it is locked. The thermal expansion of rare-gas solids being at least 10 times larger than that of substrates normally used, the distinction between floating and locked is straightforward. We show below that an unconstrained Kr monolayer adsorbed on Pt(111) thermally expands in the range $20 \text{ K} < T_s < 55 \text{ K}$ at coverages below about 0.8 monolayer (ML) like a 3D-Kr crystal (floating), while above 0.9 ML the expansion is substantially smaller corresponding to that of the Pt substrate (locked). We show further that there does exist a correlation between the locking and the buckling of the Kr layer. We show, finally, that the floating and the locked layer coexist during the phase transition, i.e., the phase transition is of first order.

The experiments have been performed in an UHV high-resolution He-scattering apparatus described in detail elsewhere.⁴ The He-beam generator and detector being immobile, i.e., $\theta_i + \theta_f = 90^\circ$, the polar diffraction scans have been taken by rotation of the crystal in the scattering plane. He-beam energies of 18.1 and 12 meV at an energy spread of $\Delta E \approx 0.25$ meV have been used. The substrate was a high-quality Pt(111) crystal with a defect density less than 0.1%. The base pressure in the target chamber with the He beam off was in the low 10^{-11} -mbar range.

All scans presented [except for Fig. 1(f)] have been obtained at constant Kr coverages. Kr was absorbed from the gas phase at pressures of $\approx 4 \times 10^{-8}$ mbar and $T_s = 25$ K. When the desired coverage was reached, the 3D Kr gas was pumped off. The results presented here

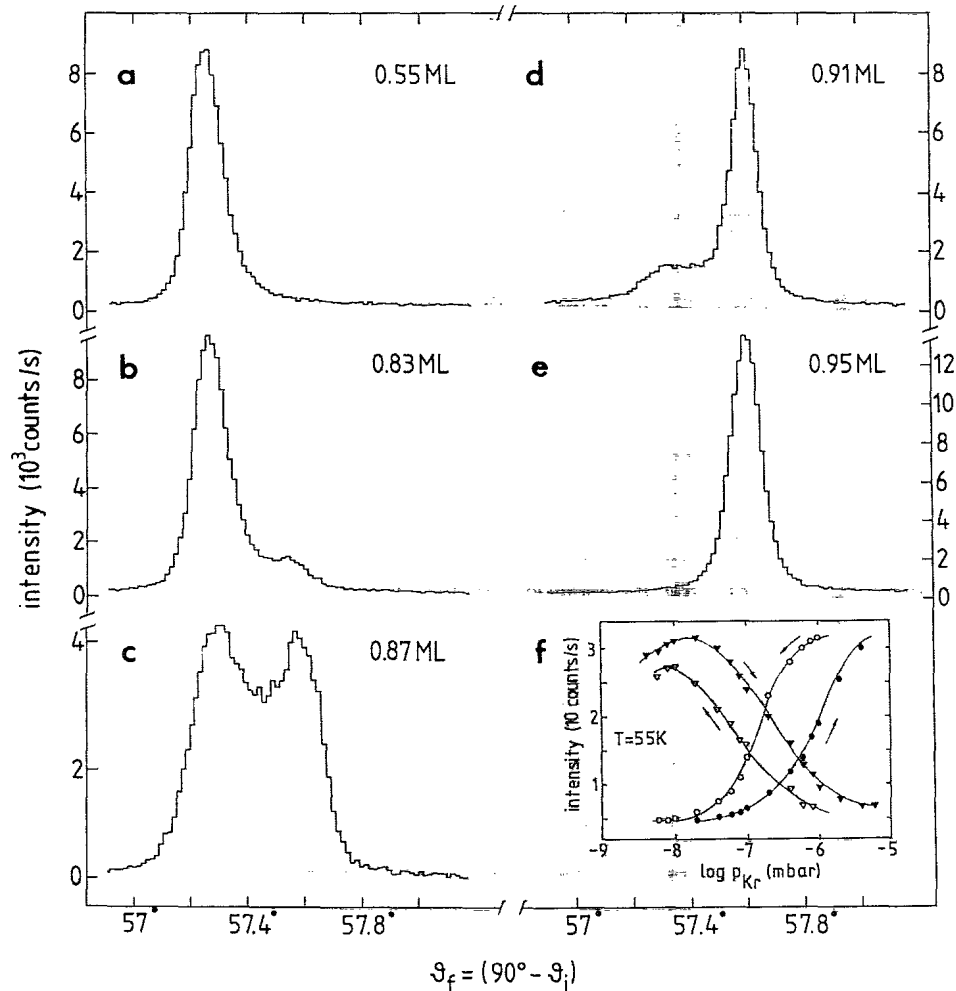


FIG. 1. (a)–(e) Polar He-diffraction scans of the $(1,1)_{\text{Kr}}$ -diffraction order at various Kr coverages and $T_s = 25$ K. (f) The intensity of the $(1,1)_{\text{Kr}}$ peak vs the equilibrium 3D-Kr pressure at constant $T_s = 55$ K; triangles, low- and circles, high-coverage phase.

are obtained with hexagonal Kr islands rotated by 30° with respect to the substrate⁵; the orientation of the hexagonal Kr layer remains unchanged up to monolayer completion [1 ML Kr on Pt(111) corresponds to 7.22×10^{14} Kr atoms/cm²]. The monitoring of the Kr coverage, in particular near monolayer completion, has been done with special care. The relative specular-He peak height, which is known to be particularly sensitive to coverage,⁶ has been used (see inset in Fig. 2). The arrow denoted by 1 ML indicates the monolayer completion. It is only beyond this point that second-Kr-layer phonons start to appear. This is a very sensitive way to determine the monolayer completion.^{2,4} Thus the thermal expansion measurements at 0.95 ML have been performed with a submonolayer, i.e., with an unconstrained Kr layer.

Figures 1(a)–1(e) show a sequence of polar scans of the $(1,1)_{\text{Kr}}$ peak monitored at 25 K, at the coverages indicated. The sequence is characteristic for a first-order

phase transition from a structure with a lattice parameter $d_{\text{Kr}} = 4.10 \pm 0.02 \text{ \AA}$ ($Q = 1.769 \text{ \AA}^{-1}$) to one with $d_{\text{Kr}} = 4.00 \pm 0.02 \text{ \AA}$ ($Q = 1.814 \text{ \AA}^{-1}$), below and above 0.8 ML, respectively. The location of the peaks remains unchanged provided the scans are monitored at the same surface temperature. During the phase transition the intensity diffracted from one phase increases at the expense of the other.

In Fig. 1(f) another type of experiment is shown: The peak height of the $(1,1)_{\text{Kr}}$ peak of each phase is plotted at constant temperature ($T_s = 55$ K) in quasiequilibrium with the 3D-Kr pressure as a function of the latter. The hysteretic behavior is obvious. This supports the first-order assignment for the phase transition.⁷ The finite slope and the somewhat broad hysteresis loop opening might be ascribed to heterogeneity effects.

The question concerning the nature of the two Kr phases, i.e., whether they are floating or locked, has been addressed by a look at their thermal expansion. In Fig. 2

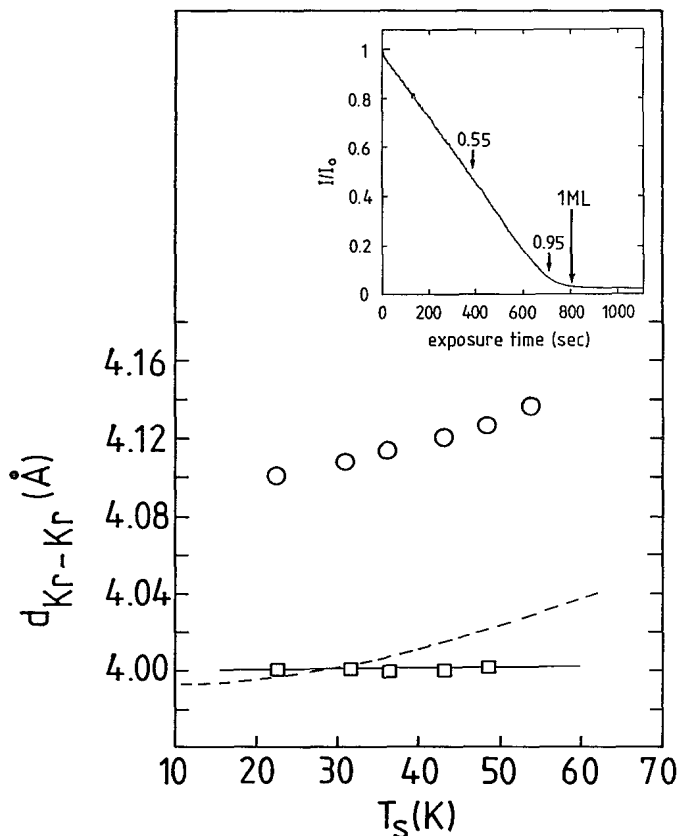


FIG. 2. Kr-lattice spacing vs T_s for squares, high- (0.95 ML) and circles, low- (0.5 ML) coverage phase; solid line, thermal expansion of the Pt substrate; dashed line, lateral spacing of Kr bulk. Inset: Specular He-peak height vs Kr exposure; see text ($T_s = 25$ K, $p_{\text{Kr}} = 9 \times 10^{-8}$ mbar).

the lattice parameter of the low- and high-coverage phases (≈ 0.5 and ≈ 0.95 ML, respectively) is plotted at constant coverage as a function of temperature. The behavior of the two phases is different. The low-coverage Kr phase expands very much like the Kr bulk and in fair agreement with the unconstrained Kr layer on Ag(111).⁸ This phase is an incommensurate floating one. In contrast, the lattice parameter of the high-coverage Kr phase is—like that of the Pt substrate—constant within experimental error in the same temperature range; this phase is thus locked on the Pt substrate. The “thermal expansion” criterion discriminates unambiguously between incommensurate floating and high-order commensurate locked phases.

Further insight into the features of the locked layer is obtained by our looking for the presence of a periodic buckling. Polar scans monitored (He-beam energy 12 meV) in the $\bar{\Gamma}\bar{K}_{\text{Kr}}$ direction of the floating and of the locked Kr layers are presented in Fig. 3. The two plots differ substantially: The locked scan clearly evidences the presence of a superstructure, while the floating one does not. The superstructure peak [the main sharp peak

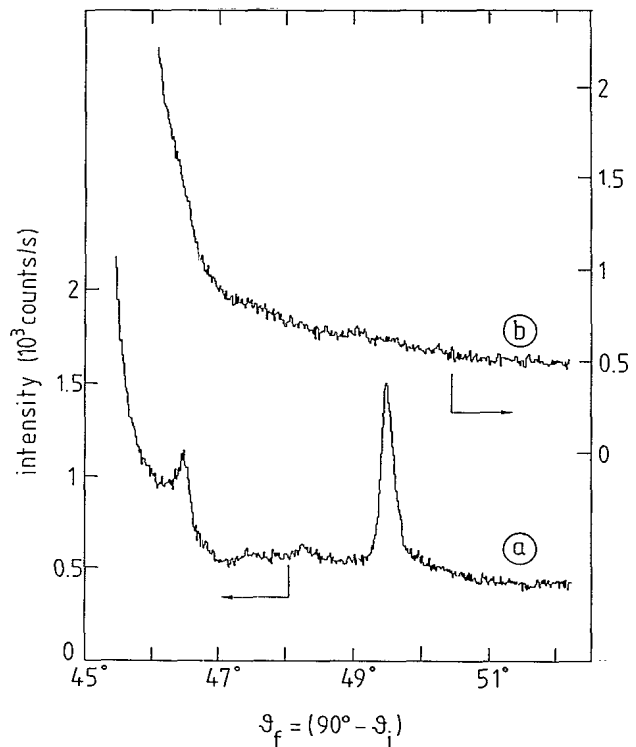


FIG. 3. Polar diffraction scans of Kr monolayers in the vicinity of the specular peak ($\theta_f = 45^\circ$); (a) high- (0.95 ML) and (b) low- (0.5 ML) coverage phase. The scattering plane was oriented along the $\bar{\Gamma}\bar{K}_{\text{Kr}}$ azimuth.

in Fig. 3(a)] corresponds to a momentum transfer of $Q = 0.532 \pm 0.022 \text{ \AA}^{-1}$.⁹

The origin of the superstructure peak seen in Fig. 3 is illustrated in Fig. 4, where the locked Kr layer (small circles; nearest-neighbor distance, $d_{\text{Kr}} = 4.00 \text{ \AA}$) lying on the outermost Pt layer (large circles; $d_{\text{Pt}} = 2.77 \text{ \AA}$) is schematically shown (the layers are assumed to be rigid). The layers are mutually rotated by 30° and their position is fixed by the locating of the central Kr atom in a high-symmetry position of the Pt substrate (say, fcc site). An inspection of the drawing confirmed by arithmetic shows that the Kr atoms in fcc sites (filled small circles) form a hexagonal (5×5) $R0^\circ$ superstructure ($d_{\text{super}} = 5 \times 2.77 \text{ \AA} = 13.85 \text{ \AA}$). The intensity of He-diffraction peaks from low corrugated hexagonal structures is known to be more than 1 order of magnitude larger in the $\bar{\Gamma}\bar{M}$ than in the $\bar{\Gamma}\bar{K}$ direction (see, for instance, Lee, Cowin, and Wharton¹⁰). This is the reason why the peak in Fig. 3 is seen in the $\bar{\Gamma}\bar{M}_{\text{super}} \equiv \bar{\Gamma}\bar{M}_{\text{Pt}} \equiv \bar{\Gamma}\bar{K}_{\text{Kr}}$ direction and is compatible with a period $\sqrt{3} \times d_{\text{super}} = 24.00 \text{ \AA}$ ($Q = 0.524 \text{ \AA}^{-1}$). The particular relation between the lattice parameters of the locked Kr layer and of the Pt substrate ($\sqrt{3} \times d_{\text{Pt}}/d_{\text{Kr}} = \sqrt{3} \times 2.77/4.00 = \frac{6}{5}$) locates the same number of Kr atoms in hcp sites (shaded small circles). The superstructure formed by the Kr atoms in fcc and hcp sites has the

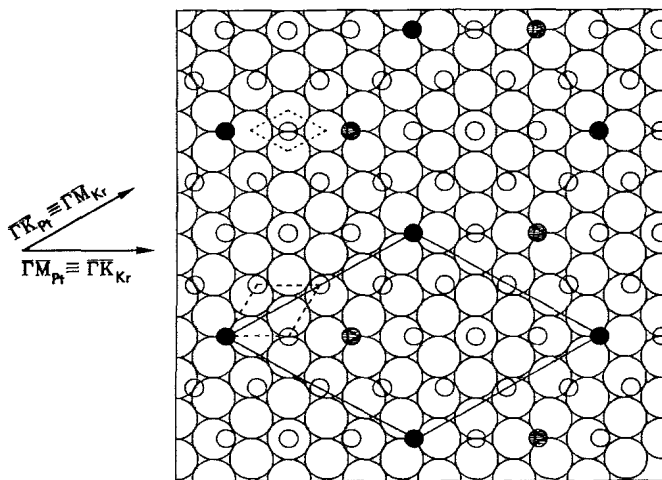


FIG. 4. Schematic representation of the high-coverage phase of Kr on Pt(111).

same $(5 \times 5)R0^\circ$ symmetry except for the unit cells now containing two Kr atoms, one in an fcc and the other in an hcp site.

The correlation between thermal-expansion behavior (Fig. 2) and presence or absence of a periodic adlayer buckling (Fig. 3) is obvious. The Pt-type expansion and the periodic adlayer buckling at high coverage are both due to a fraction of the Kr adatoms being locked at high-symmetry sites of the substrate: The high-coverage Kr layer is locked because it is a (high-order) commensurate phase. On the other hand, the high- and low-coverage layers both being oriented along high-symmetry axes of the substrate ($R30^\circ$), there is no reason for a static distortion of "the monolayer which appears as a consequence of the rotation"³ to be present. Thus there is no superstructure peak in Fig. 3(b) and the peak in Fig. 3(a) does originate from the particular location of a fraction of the Kr atoms in fcc and hcp sites as shown in Fig. 4.

A simple counting in Fig. 4 shows that one out of six Kr atoms is locked in an fcc or hcp site of the substrate. These atoms appear to be sufficient to hinder the Kr layer from expanding freely, by constraining it at the low thermal expansion of the Pt substrate over at least 25 K (Fig. 2). This observation emphasizes the actual reason for the surprising inability of molecular-dynamics calculations¹¹ to predict the existence of the $(\sqrt{3} \times \sqrt{3})R30^\circ$

Xe layer on Pt(111), which has been observed to be perfectly stable in a broad range of temperatures and coverages¹². The potential corrugation for rare gases adsorbed on close-packed metal surfaces is much larger than considered so far in theoretical work. Apparently the very low corrugation of the repulsive potential of close-packed metal surfaces inferred from *He-scattering* experiments cannot be extended to the corrugation of the bottom of the potential well felt by the *heavier* rare gases adsorbed on these surfaces. This latter corrugation has been measured directly for Xe on W(110)—a rather close-packed surface—by the field-emission current-fluctuation method.¹³ The obtained value, $E_{\text{dif}}=47$ meV ($=545$ K) is about 1 order of magnitude larger than the value postulated in theoretical calculations.¹¹

In summary, we have uncovered the existence of a phase transition between an incommensurate and a high-order commensurate 2D layer. The phase transition is first order. The distinction between an incommensurate floating and a high-order commensurate locked-in layer has become possible by use of a new and, we feel, a very strong criterion: the thermal expansion behavior.

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