# Impurity-Quenched Orientational Epitaxy of Kr Layers on Pt(111)

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The assumption that minute defects and impurities may be the cause for discrepancies between experiment and theory on physisorbed films is confirmed for the first time in direct experiments. A change of 30° in the orientation of a Kr layer on Pt(111) induced by H and CO precoverages as low as 0.1%, via the blocking of step sites, is demonstrated by high-resolution He diffraction.

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The failure of even careful experiments to confirm definite theoretical predictions concerning salient features of physisorbed layers is often assigned to an excessive sensitivity substrate impurities and defects. For instance, by application of Novaco and McTague's analysis to Xe/Ag(111), Bruch and Phillips have predicted that the Xe layer has to be rotated by approximately 30° with respect to the Ag lattice.[1] However, in all experiments performed before[2,3] and after[4] the work of Bruch and Phillips, the Xe lattice is observed to be aligned with the Ag lattice. Although the reason for this contradiction was not known, it has been attributed to defects on the surface.[2,3] This assignment seems to be supported by theoretical considerations.[1]

Recently, Villain and Gordon[5] have analyzed the extent to which impurities and other defects may contribute to the discrepancies. In the case of the commensurate-incommensurate (CI) transition of Kr layers on graphite (Gr) they concluded that impurity effects can explain a number of features, as for instance that "the striped phase was never found[5]" in experiments. On the other hand, our very recent experimental data demonstrate that the striped phase does show up during the CI transition of Xe on Pt(111).[6] Similarly, the CI transition at constant coverage predicted by Gordon and Villain[7] to take place at $T_{\mathrm{CI}} \simeq 34$ K for Kr/Gr has been found to take place for Xe/Pt(111) at $T_{\mathrm{CI}} \simeq 62$ K[8] but not yet on Kr/Gr. The systems Kr/Gr and Xe/Pt(111) have striking similarities,[8] but—and this seems to confirm Villain and Gordon's conclusion—the Pt(111) surface can be prepared to a very high degree of perfection: By refined procedures the density of defects and impurities on the Pt(111) surface is reduced below 0.1%.[9,10] On the other hand, it has also been suggested that the azimuthal orientations of the $\zeta'$ and $\zeta$ structures of $O_2$/Gr differ because the former is caused by steps present on the Gr crystal.[11]

This all suggests strongly that defects and impurities may indeed influence the properties of physisorbed layers, but it is still only indirect evidence. There is, to the best of our knowledge, no experiment which has demonstrated that a given salient feature of a physisorbed layer may be radically changed by impurity coverages of far less than $\theta = 1\%$, which are beyond the detection limit of most surface-analytical techniques. It is the purpose of this Letter to present the experimental proof for such an excessive sensitivity. We will show that the orientation of a Kr layer deposited on a Pt(111) surface precovered with $\theta \leq 0.2\%$ of impurities (H,CO) is changed by not less than 30° with respect to the orientation of a Kr layer deposited on the nonprecovered, clean Pt(111) surface. Because such a low impurity level has inevitably been overlooked even in the most careful experiments performed so far, these findings are particularly relevant to the assessment of the discrepancies between theory and experiment.

The choice of the Kr/Pt(111) system has been based on the following considerations. The examples mentioned above suggest that the Pt(111) surface can be prepared to a condition which satisfies the ideality requirements of the theory in the case of physisorbed layers. On the other hand, Kr/Pt(111) has similarities with the system Xe/Ag(111) for which, as already mentioned, a ~30° orientation discrepancy between theory[1] and experiment[2-4] has been observed. In particular, both layers exhibit an incommensurate hexagonal structure; the misfit with respect to the $\sqrt{3}$ lattice parameter of the substrate and the various heats of adsorption are not dramatically different.[12] Bruch and Phillips[1] have demonstrated that the "shape function" $\Sigma$, whose maximum determines the orientation of the layer, is only a function of the ratio $L/l$ of the layer and substrate nearest-neighbor distances, respectively. The $L/l$ values for unconstrained submonolayers of Xe/Ag(111) and Kr/Pt(111) at 25 K are 1.536 and 1.476, which corresponds to $\sqrt{3}$ misfits of 11.3% and 14.8%, respectively. The layer orientation relative to the substrate expected according to Eq. (2.11) in Ref. 1 is 25.1° and 23.2°, respectively. In Bruch and Phillips's[1] terminology the orientation should be within 5° and 7°, respectively, of 30°.

The results presented here have been obtained in a high-resolution He-scattering UHV apparatus, described in detail by David *et al.*[13] High-resolution He scattering appears ideally suited for the kind of investigations reported here. Scattering of thermal-energy He atoms supplies, besides sharp and simple diffraction patterns (see below), accurate information on the presence of steps,[9] impurities, and even individual surface defects[14] at concentrations down to 0.1%. In addition, the interaction of thermal He atoms with the surface is completely nondestructive, which is of particular importance in the case of rather delicate physisorbed layers.

The Kr layers have been obtained here by our exposing the clean or precovered Pt(111) surface at $T_s = 25$ K to a Kr pressure of $4\times10^{-8}$ mbar for 30 s and then pumping the Kr off. This leads to a coverage $\theta_{\mathrm{Kr}} \simeq 0.1$ (with $\theta_{\mathrm{Kr}} = 1$ corresponding to $1.5\times10^{15}$ atoms/cm$^2$). Because the Kr-Kr interaction is attractive and the Kr atoms are mobile at 25 K on the Pt(111) surface, islands with an ordered hexagonal structure are formed. Annealing up to 50 K improves the order slightly. Essentially similar results are obtained in the whole coverage range up to Kr-monolayer saturation at about $\theta_{\mathrm{Kr}} \simeq 0.5$. For the work described in this paper, we have used Kr coverages of 0.1 for two main reasons. First, we sought to achieve a fully unconstrained layer, in order to avoid the influence on the orientation of the layer of undefined parameters. Second, at these low Kr coverages, with about 80% of the Pt surface being uncovered, the $(1,1)_{\mathrm{Pt}}$ diffraction peak of the clean Pt(111) surface is always present. This peak is very useful for exact substrate orientation, He wavelength calibration, and instrumental function recalibration in the presence of the Kr submonolayer. On this basis, the Kr-layer azimuthal orientation, lattice parameter, and average island size are straightforwardly determined (see, e.g., Ref. 13). The lattice parameter and average island size of the various layers ($\theta_{\mathrm{Kr}} = 0.1$) were equal within the experimental accuracy: $4.10 \pm 0.02$ and ~70 Å, respectively. The orientation of the Kr layers, the key issue of this Letter, is discussed in detail below.

In order to facilitate the discussion, we show in the insets in Figs. 1(a) and 1(c) a 30° sector of the reciprocal lattice with the pertinent notations for the two azimuthal orientations of the Kr layer observed in the present experiment: the 30°-rotated ($R30°$) and the aligned layer ($R0°$), respectively. The reciprocal-lattice points of Kr and Pt are denoted by open squares and open circles, respectively. A common feature of the smooth (111) faces of fcc metals and of incommensurate noble-gas layers grown on them is that the He-diffraction patterns consist practically only of peaks in the $\overline{\Gamma}\overline{M}$ direction $(n,n)$. We have denoted them by closed points and closed squares. The peaks in the $\overline{\Gamma}\overline{K}$ direction, being hardly detectable above the noise level, have been denoted by open symbols. This simplifies the question addressed here of the orientation of the layer with respect to the substrate.

The structure—and, in particular, the orientation of the Kr layer adsorbed on the clean Pt(111) substrate—is fully characterized by the diffraction patterns in Figs. 1(a) and 2(a). The azimuthal plot in Fig. 1(a) is taken at the polar angle of the $(1,1)_{\mathrm{Kr}}$ peak along the dashed arrow in the inset. It shows only one strong peak at the $\overline{\Gamma}\overline{K}_{\mathrm{Pt}}$ azimuth but no intensity at the $\overline{\Gamma}\overline{M}_{\mathrm{Pt}}$ one. The polar plot in Fig. 2(a), taken in the $\overline{\Gamma}\overline{K}_{\mathrm{Pt}}$ direction of the substrate, shows two sharp peaks at the $(1,1)_{\mathrm{Kr}}$ and $(2,2)_{\mathrm{Kr}}$ positions. Polar scans taken in the $\overline{\Gamma}\overline{M}_{\mathrm{Pt}}$ direction of the substrate (not presented here) show only a very weak $(1,2)_{\mathrm{Kr}}$ diffraction peak ($I_{(1,2)}/I_{(1,1)} \simeq 3\times10^{-3}$). A comparison with the inset demonstrates that this Kr layer adsorbed on a nearly perfect Pt(111) surface is rotated by 30° ($R30°$) with respect to the substrate and not aligned ($R0°$) as for Xe on Ag(111).

In order to obtain the almost impurity- and defect-free surface, which supplies diffraction patterns like those in

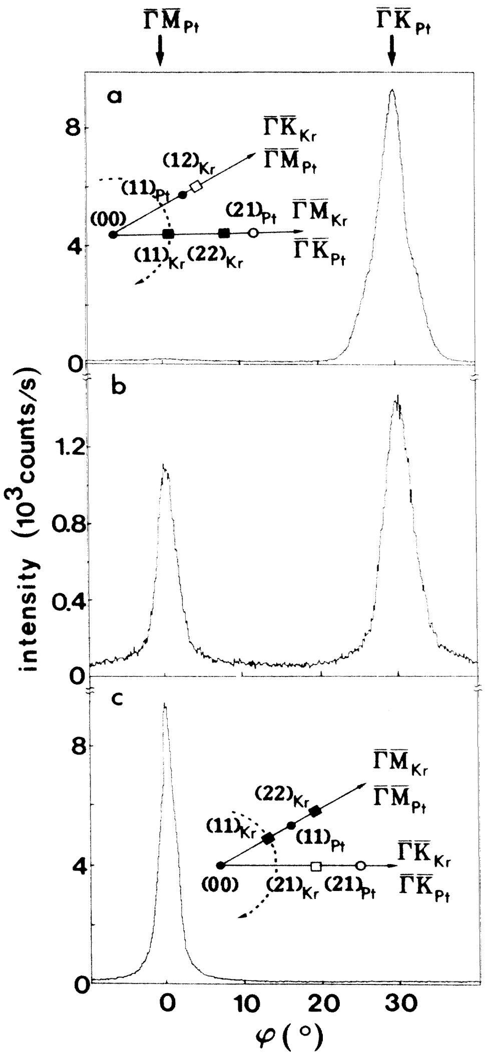

FIG. 1. Azimuthal scans of He-diffraction patterns monitored along the directions indicated by the dashed arrows shown in the insets, and of Kr layers ($\theta_{\mathrm{Kr}} \simeq 0.1$) deposited on an almost defect-free (<0.1% step atoms) Pt(111) surface with various H precoverages: (a) *no* precoverage; (b) $\theta_{\mathrm{H}} < 0.1\%$ and (c) $\theta_{\mathrm{H}} \simeq 0.2\%$ precoverage on the (111) terraces, i.e., partial (b) and, respectively, full (c) coverage of the step sites.

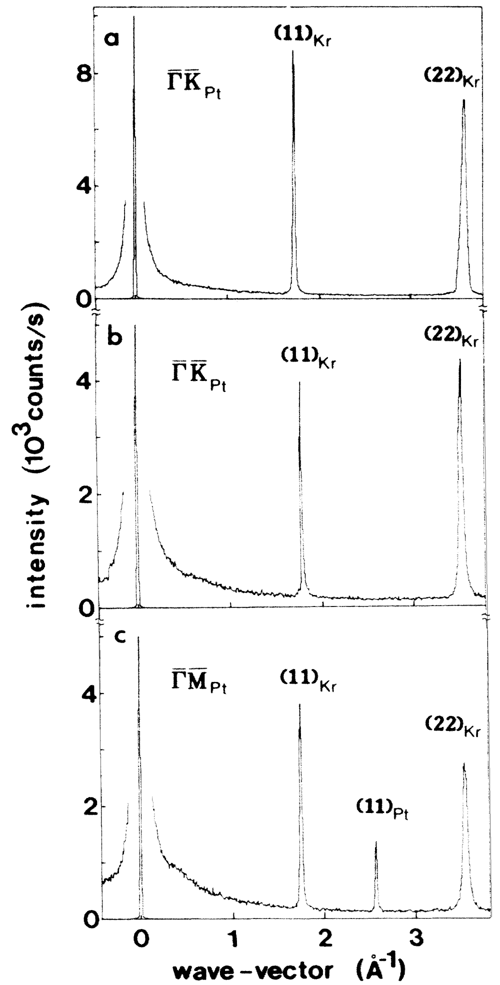

FIG. 2. Polar plots monitored in the indicated azimuths from Kr layers as in Fig. 1, but with different kinds of CO precoverages: (a) *no* precoverage; (b) and (c) same amounts of CO precoverage ($\theta_{CO} \simeq 0.1\%$), but in (b) distributed randomly on step and terrace sites, while in (c) concentrated on step sites. The specular peak heights ($Q = 0$ $Å^{-1}$) are multiplied by factors of $2.5 \times 10^{-3}$ (a) and $1.25 \times 10^{-3}$ [(b) and (c)], respectively.

Figs. 1(a) and 2(a), careful and often tedious cleaning and annealing procedures at base pressures in the low $10^{-11}$-mbar range must be carried out. The crystal is first oriented, cut, and polished as described in detail in Ref. 9. Then, cycles of chemical cleaning by our heating the surface to 800 K in an oxygen atmosphere of $10^{-6}$ mbar and sputtering with $Ar^+$ (900 eV) and $Xe^+$ (600 eV) ions followed by short annealing at 1000 K are alternatively performed. At the point where the surface is characterized as clean and well ordered by surface-analytical methods, i.e., when the level of impurities and defects has reached the detection limit of, e.g., Auger electron spectroscopy and low-energy electron diffraction and even of specular He scattering (~0.1%), the He diffraction pattern of the adsorbed Kr layer is far from looking like that in Figs. 1(a) and 2(a). Only by continuation of the cleaning and annealing procedures far beyond this point does the "ideal" diffraction pattern emerge. It seems that the "Kr criterion" for the Pt(111) surface perfection is superior to the present analytical techniques.

The decisive proof for the dramatic influence of minute impurities on the Kr-layer orientation is given by the succession of the three azimuthal plots in Fig. 1. All three plots are taken at the polar angle of the $(1,1)_{Kr}$ peak along the dashed arrows in the insets. The Kr layers have been grown by use of identical Kr exposures on an identically prepared surface but with different hydrogen precoverages. In case (a), as already mentioned the surface has been exposed to Kr *without* H precoverages. In case (b) the preexposure to hydrogen was obtained by the opening and immediate closing of the $H_2$ leak valve; the $H_2$ pressure increased to a few $10^{-10}$ mbar and fell immediately. The hydrogen adsorbed resulted in no measurable decrease of the He reflectivity, i.e., the hydrogen coverage on the Pt(111) terraces was $\theta_H \leq 0.1\%$. In case (c) the hydrogen leak valve was kept open a couple of seconds resulting in a measurable decrease, $5 \times 10^{-3}$, of the He reflectivity, i.e., in a H coverage at the terraces of $\theta_H \simeq 0.2\%$.

The changes in Fig. 1 are dramatic. In view of the fact that the H-binding energy is ~120 meV larger on step than on terrace sites and that H is fully mobile the following assessment of the observations can be made: (a) no H precoverage → only *R*30° Kr domains present; (b) a H precoverage leading only to a partial coverage of the step sites (no measurable terrace coverage) → decrease of the total area of *R*30° Kr domains and the appearance of *R*0° Kr domains; (c) a terrace coverage of $\theta_H \simeq 0.2\%$, i.e., the *full* coverage of the step sites → *complete* disappearance of rotated domains, the whole Kr layer being aligned. Note that the corresponding polar plots (not shown here) demonstrate that neither the lattice parameter nor the average island size of the Kr layer changes measurably upon H precoverage; the relatively smaller azimuthal widths of the aligned peaks in Figs. 1(b) and 1(c) indicate that the aligned layer is angularly better locked. Note further that neither H postexposure nor annealing of the various Kr layers change the picture shown so far.

The general conclusion is that the assertion that hardly detectable minute amounts of impurities and defects may change dramatically properties of physisorbed layers is correct. However, the particular mechanism assumed to lead to the "alignment" of Xe on Ag(111) (the Xe domain size reduction by impurities[1]) seems not to work for Kr/Pt(111), where no domain size change is observed. Actually, the behavior illustrated in Fig. 1 rather suggests that the blocking of step sites might play a decisive role. This has been confirmed by the use of CO instead of H precoverages.

We have chosen CO because the location of CO molecules can be manipulated in the accessible temperature range ($T_s > 25$ K). Indeed, when adsorbing CO at a surface temperature, where it is immobile upon adsorption [$T_s < 150$ K on Pt(111)[14]], the molecules stay randomly distributed over terrace and step sites with densities roughly equal to the overall coverage of say $\theta_{\mathrm{CO}} \simeq 0.1\%$. On the other hand, by adsorption of the same amount of 0.1% CO at $T_s > 170$ K, the molecules migrate and are eventually bound at step sites, where they remain upon cooling. Since the step density is $\leq 0.1\%$, the coverage of the step sites becomes $\theta_{\mathrm{CO}} \simeq 1$, i.e., the step sites are completely blocked by CO. Polar scans of He diffracted from Kr layers deposited on these two "types" of CO precoverage are shown in Figs. 2(b) and 2(c). Figure 2(b) illustrates that randomly distributed CO has no influence on the Kr-layer orientation, which is still $R30°$. Indeed, plot (b) has been taken like plot (a) in the $\bar{\Gamma}\bar{K}_{\mathrm{Pt}}$ direction and no new peaks have appeared; in particular there is no diffracted intensity in the $\bar{\Gamma}\bar{M}_{\mathrm{Pt}}$ direction. If, however, CO fully blocks the step sites the situation is exactly reversed, all the diffracted intensity is in the $\bar{\Gamma}\bar{M}_{\mathrm{Pt}}$ and no intensity in the $\bar{\Gamma}\bar{K}_{\mathrm{Pt}}$ direction, i.e., the Kr layer is now aligned ($R0°$) with the Pt(111) substrate as in the case of H preadsorption. This is illustrated in the polar scan (c) which is now taken in the $\bar{\Gamma}\bar{M}_{\mathrm{Pt}}$ direction: Note the presence of the $(1,1)_{\mathrm{Pt}}$ diffraction peak, which must obviously be present in this direction [see inset in Fig. 1(c)].

The results in Fig. 2 demonstrate that a given minute ($\sim 0.1\%$) amount of CO precoverage influences radically the Kr-layer orientation only if it is concentrated at the steps. This is a direct proof for the fact that impurities influence the Kr-layer orientation by blocking of the step sites. One may infer further that the $R30°$ Kr layer orientation observed on the *nonprecovered* surface is due to the preferential orientation of the Pt step rows (probably ⟨110⟩) on which the Kr atoms are bound first, creating nucleation centers for the growing of 2D islands. When the step sites are blocked by H or CO, the Kr islands nucleate apparently on the free (111) terraces and grow with an orientation $R0°$.

In summary, the discrepancies between theory and experiment may indeed be due to the presence of hardly detectable defects and impurities. However, because defects can never be completely avoided and because adatoms are always bound at nonblocked step sites, the salient features of the layer may be decisively influenced in many cases by the kinetics of the layer growth with defects as nucleation centers. This ought to be given theoretical consideration.

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