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High Resolution He-Scattering Studies of Physisorbed Films

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In bulk matter, the local icosahedral clustering of twelve atoms around a central particle is significantly denser than in the corresponding hcp or fcc clusters ^{1/1}. However, icosahedra cannot be stacked to fill completely the 3D space; i.e. no solids with long range order can be formed with icosahedral units. Thus, three dimensional crystals with perfect long range order do not reach the maximum attainable short range density. These competing trends lead to a variety of interesting phenomena: like the fascinating matter of quasicrystals ^{2/2}. In two dimensions, the densest possible local arrangement around a central particle is the hexagon. Obviously, hexagons can form a close packed 2D-solid with long range order. Thus, in contrast to the 3D case, in two dimensions the requirements for maximum long range order and maximum short range density are identical. At first glance, this coincidence seems to reduce the "physical interest" in two dimensional systems substantially. However, it turned out that enhanced fluctuation effects due to the reduced dimensionality lead to novel and quite subtle phenomena in these systems. In addition, fascinating aspects arise from the fact that (in experiment) 2D-solids need to be supported by a substrate: in model 2D-systems, the 2D-layer is physisorbed on a single crystal surface. The physisorbed atoms form a modulated structure on the lattice of the substrate surface. The modulation arises from the competing interactions which favor different periodicities, the nearest-neighbor distance preferred by the lateral adatom interaction differs in general from the lattice periodicity which the substrate potential tries to impose. Such modulated systems display a great richness of phases and of phase transitions when the conditions of coverage and/or temperature are varied, and thus have attracted much theoretical ^{3/3} and experimental ^{4/4} interest.

A variety of probe particles, e.g. electrons, neutrons, X-ray photons and thermal atoms are used as structural tools of physisorbed films. All methods have their pros and cons. Low energy electron diffraction (LEED), for instance, is the most accessible technique, but suffers from the consequences of the strong interaction of the electrons with the adsorbed layer (multiple scattering, electron stimulated desorption etc.). Synchrotron X-ray scattering, on the other hand, has an excellent momentum resolution, but is hampered in application by the low surface sensitivity.

We will demonstrate here the unique capabilities of high resolution He-scattering in investigating physisorbed adlayers, with particular emphasis on structural aspects. Among the probe particles mentioned above, none causes less disturbance of the system under investigation than thermal neutrons and thermal He-atoms. In the case of He-scattering this property is associated with a sensitivity confined to the outermost layer (no penetration into deeper layers). Within an easily accessible source temperature range the He-atom wave length is well suited for diffraction at crystal surfaces, and its energy allows for high resolution measurements of collective lattice excitations. In addition, the diffuse scattering of He atoms is very sensitive to surface disorder. This technique has certainly also limitations. The most severe appears to be the restriction to ambient pressures below 10^{-6} mbar, making interesting parts of phase diagrams inaccessible. Some limi-

tation in momentum resolution (presently $\Delta O/Q \sim 0.01$) might be overcome in the next generation of instruments.

The high resolution He-scattering spectrometer used in the studies of physisorbed films has been described in detail in ref.5. Here, we briefly remind the basic features. The target is a high quality Pt(111) surface with an average terrace width of about 3000Å. The crystal is mounted in an ultrahigh vacuum chamber, with a base pressure in the low 10^{-10} -mbar range, on a manipulator that allows independent polar and azimuthal rotation and tilting. The temperature of the crystal can be regulated between 25K and 1800K. The temperature is measured with a chromel-alumel thermocouple, spot-welded to the crystal, and calibrated *in situ* via the measurement of the Xe-3D vapor pressure by means of surface phonon spectroscopy ^{5/6/}. The measurements are performed at fixed total scattering angle, $\theta + \theta_i = 90^\circ$. The angular spread of the incident beam and the angle subtended by the detector opening are both 0.2° . The majority of measurements are performed with a liquid nitrogen cooled nozzle, generating a 18.3 meV He-beam ($\lambda = 1.062\text{Å}$) with an energy spread $\Delta E = 0.25\text{meV}$ ($\Delta\lambda/\lambda = 0.007$).

A central aspect of the 2D-systems consists of the commensurate and incommensurate phases and their mutual transitions. An adsorbed layer is defined as commensurate, if its basis vectors result from a rational combination of the basis vectors of the substrate. According to this definition, the substrate vectors are irrational, the adlayer is incommensurate. According to this definition, a certain fraction of the commensurate layer atoms is located in equivalent substrate sites (eg. in high symmetry three fold hollow sites of the (111) surfaces of fcc crystals or hexagon centers of the basal plane of graphite); if this fraction is unity, i.e. all layer atoms are located in equivalent sites the layer is simply named commensurate, otherwise "high order" commensurate. Obviously, the atoms located in equivalent sites form a periodic structure, a superstructure. A basic property of all commensurate layers is that they have discrete rather than continuous symmetry and that infinitesimal displacements of the whole layer costs a non zero amount of energy, i.e. in principle the commensurate layers are "locked" on the substrate. Lock-in transitions in modulated systems have been matter of intensive theoretical consideration ^{3/3}. One of the most fascinating results was that of Aubry's zero temperature theory which suggested that the wavevector will lock in to all commensurate wavevectors, and that there are no incommensurate phases in between ^{7/7}. Thus, the wavevector varies continuously, but nonanalytically; a form which is known as *devil's staircase*. The notion of devil's staircase is somewhat academic because most of the wavevector steps are narrow and because finite temperature effects have been neglected. The layers are only locked, i.e. can be regarded as high order commensurate, if the energy gain due to the partial occupation of preferred adsorption sites is large compared to the characteristic energies of the vertical excitations of the adatoms (which are typically between 30 and 50K).

Until very recently, there has been no convincing experimental evidence for the existence of high order commensurate physisorbed layers. This appeared to support the widespread belief that "experimentally it is impossible to distinguish between a high order-C structure and an incommensurate structure" (Per Bak in ref.8, p.590).

This belief is certainly legitimate, if the only accessible experimental information is the ratio of the adlayer and substrate lattice basis vectors. Indeed, because one can find always one rational number within the confidence range of any experimental irrational number, i.e. the basis vectors supplied by the most refined experiment are always compatible with a high (enough) order

commensurate phase. There are, however, two other experimentally accessible parameters which allow a unequivocal distinction between a high order commensurate "locked" and an incommensurate "floating" layer. First: the superstructure formed by the atoms located in equivalent, high symmetry sites. These stronger bound atoms being located "deeper" in the surface than the others, the adlayer is periodically buckled. Because of the extreme sensitivity of He-scattering to the surface topography, this superstructure, which characterizes high order commensurate layers, is directly accessible to a high resolution He-diffraction experiment. As shown further below, these superstructures can be distinguished from those resulting from mass density waves (MDW) appearing in Novaco-McTague rotated layers. Second: the thermal expansion. Indeed, a "floating" layer is expected to thermally expand very much like the corresponding rare gas bulk crystal, while a "locked" layer has to follow by definition the substrate at which it is locked. The thermal expansion of rare gas solids being at least ten times larger than that of substrates normally employed, the distinction between high order commensurate "locked" and incommensurate "floating" becomes straightforward. This very sharp criterion requires that the "locking" is strong enough to withstand temperature variations over a sufficiently large range ($\geq 10K$) to allow for reliable thermal expansion measurements.

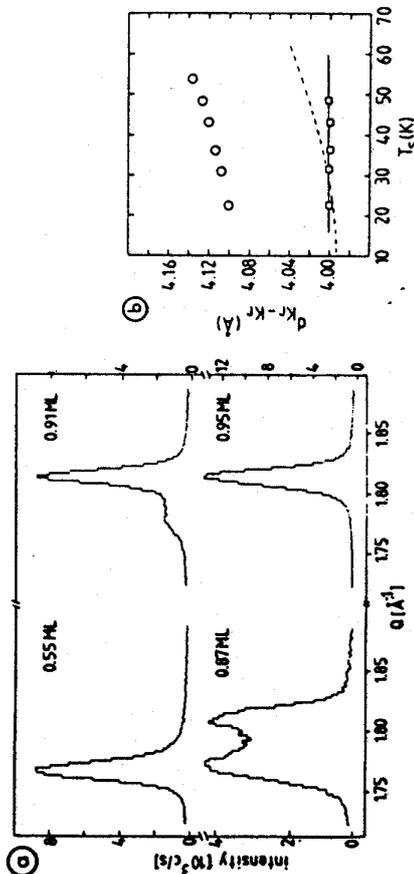


Fig. 1: a) Polar He-diffraction scans of the $(1,1)_{Kr}$ -diffraction order from Kr adlayers on Pt(111) at various Kr submonolayer coverages at $T_s = 25K$. b) Kr-layer lattice spacing vs T_s for the (O) high (0.95 ML) and (o) low (0.5 ML) coverage phase; temperature dependence of the lattice spacing of (----) Pt-substrate, and of (- - -) bulk Kr

Figure 1a shows a series of polar He-scans of the $(1,1)_{Kr}$ diffraction peak taken at 25K along the $\bar{\Gamma}M_{Kr}$ direction of the Kr monolayers adsorbed on a Pt(111) surface at coverages between 0.5 and 0.95 ML. The sequence is characteristic for a first order phase transition from a hexagonal solid phase with wavevector $Q = 1.769\text{\AA}^{-1}$ ($d_{Kr} = 4.10\text{\AA}$) to one with $Q = 1.814\text{\AA}^{-1}$ ($d_{Kr} = 4.00\text{\AA}$), below and above 0.8 ML, respectively. During the phase transition the intensity diffracted from one phase increases at the expense of the other.

The question concerning the incommensurate "floating" versus high order commensurate "locked" nature of the two Kr-phases has been addressed by looking at their thermal expansion

behavior and by searching for superstructure satellites. In fig. 1b the measured Kr-Kr interatomic spacing versus temperature is shown for submonolayer films of coverage 0.5 ML and 0.95 ML. The difference is striking. The low coverage phase shows a variation with temperature, very much like bulk Kr (dashed) and is thus an incommensurate "floating" phase. On the contrary, the lattice parameter of the high coverage phase is - like that of the Pt substrate (solid) - constant within experimental error in the same temperature interval; accordingly, this Kr-phase thus is high order commensurate "locked".

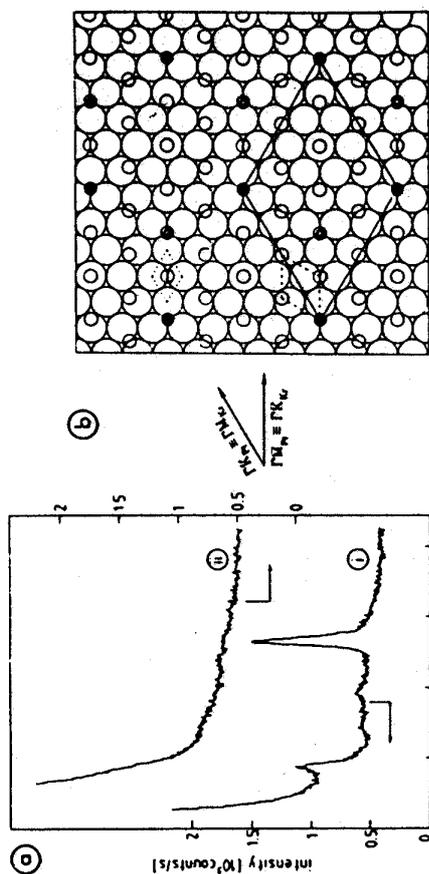


Fig. 2: a) Polar He diffraction scans of Kr monolayers in the vicinity of the specular peak ($Q = 0\text{\AA}^{-1}$); i) high (0.95 ML) and ii) low (0.5 ML) coverage phase, taken along the $\bar{\Gamma}K_{Kr}$ -azimuth. b) Schematic representation of the high coverage phase of Kr on Pt(111); small circles represent Kr-atoms ($d_{Kr-Kr} = 4.00\text{\AA}$) while large circles the Pt substrate atoms ($d_{Pt-Kr} = 2.77\text{\AA}$)

This assignment is supported by inspection of fig. 2, where polar scans (He-beam energy 12 meV) in the $\bar{\Gamma}K_{Kr}$ -direction of the "floating" and of the "locked" Kr-layer are shown. The scans differ substantially: the locked scan clearly evidences the presence of a superstructure, while the floating one does not. The superstructure peak at $Q = 0.532 \pm 0.022\text{\AA}^{-1}$ corresponds to 1/5 of the Pt-substrate principal lattice vector. The origin of the superstructure peak is illustrated on the right hand of fig. 2 where the "locked" Kr-phase on the Pt(111) surface is schematically shown. The Kr-layer is rotated by 30° with respect to the substrate and its translational position is fixed by locating the central Kr-atom in a preferred three fold hollow site (say fcc). Obviously, the Kr-atoms in fcc-sites (filled small circles) form a hexagonal $(5 \times 5)R0^\circ$ -superstructure, which is responsible for the diffraction satellite at $Q_{\parallel}^{(1)}/5$. Note, that the superstructure is aligned with the substrate lattice while the Kr-layer as a whole is rotated by 30° ; this is the reason while the superstructure satellite is seen in the $\bar{\Gamma}M_{Kr} = \bar{\Gamma}K_{Kr} = \bar{\Gamma}M_{superstructure}$ -direction. The particular ratio between the lattice parameters of adlayer and substrate $\sqrt{3} d_{ad}/d_{Kr} = 8/5$ produces an additional peculiarity; the same number of Kr-atoms are located in hcp- and fcc-hollow sites. Thus, the $(5 \times 5)R0^\circ$ -superstructure has a two-atomic basis. A simple counting in fig. 2 shows that one sixth of the Kr-atoms is locked in a hollow site (fcc or hcp). This fraction appears to be sufficient to hinder the Kr-layer to expand freely over more than 25K.

The correlation between negligible thermal expansion and presence of a periodic adlayer buckling in the high coverage phase of Kr on Pt(111) unequivocally demonstrates the high order commensurate character of this phase. The superstructure peak in fig. 2 originates certainly from the layer buckling due to a fraction of Kr atoms located in high symmetry sites of the substrate. Indeed, the Kr layers being oriented along high symmetry axes of the substrate, there is no reason for the occurrence of mass density wave satellites (see below) which might complicate the interplay /9/.

However, the situation is different for adlayers in which the high symmetry directions of adlayer and substrate are noncollinear. The occurrence of the rotation of adlayers away from the substrate symmetry directions as a function of relative lattice misfit has been predicted theoretically by Novaco and McTague /10/. Since transverse strains have lower energy than longitudinal strains in a 2D-layer, the interconversion of these strains can favor a tilt of the adlayer symmetry axes. Novaco and McTague have been able to show that this phenomenon involves the creation of mass density waves, MDW, (also known as static distortion waves, SDW). These MDW bear relevant similarities with the charge density waves (CDW) of layered crystals. Indeed, it is the combination of rotation and small displacive distortions of the adatom net which allows the adlayer to reach its lowest energy in the potential relief of the substrate surface. In a diffraction experiment, these mass density waves should give rise to additional satellites.

Fuselier et al. /11/ have introduced an alternative concept to explain the adlayer rotation: the "coincident site lattice". They pointed out that energetically more favorable orientations are obtained for rotated high order commensurate structures. The larger the fraction of adatoms located in high symmetry sites, the larger the energy gain and the better the rotated layer is locked. It turned out that the predictions of the coincident site lattice concept for the rotation angle versus misfit agrees well with the Novaco-McTague predictions.

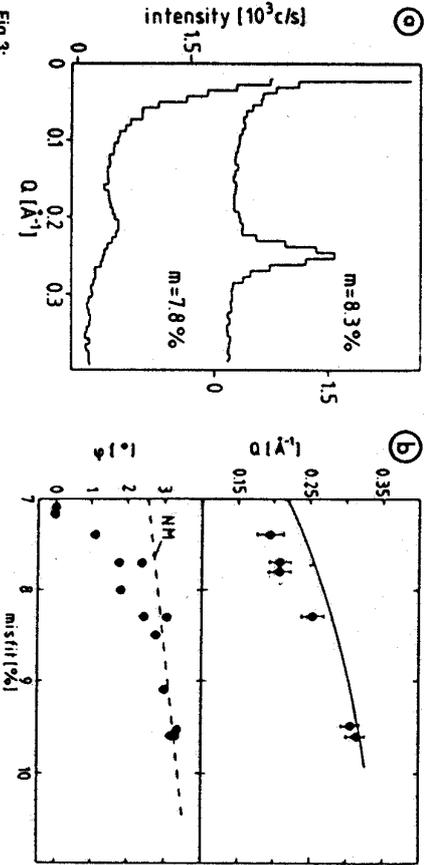


Fig. 3: a) Polar He-diffraction scans of rotated Xe monolayers on Pt(111) in the vicinity of the specular peak ($Q = 0\text{\AA}^{-1}$) taken along the $\vec{\Gamma}\bar{M}_x$ -azimuth, at $m = 7.8\%$ and 8.3% , respectively. b) Dispersion of the mass density wave (MDW) satellites with misfit m . The solid line is Gordons relation (eq. 1). Also shown is the variation of rotation angle φ vs misfit m .

In the He diffraction patterns from a Novaco-McTague related monolayer, Xe on Pt(111), we have also observed satellite peaks, and assigned them to a commensurate buckling /12/. However, Mirra Gordon /9/ pointed out that these satellites could be due to the MDW. Here, we will show that, indeed, both MDW as well as commensurate buckling satellites are present in the rotated Xe monolayers on Pt(111). The distinction between the two types of satellites is straightforward. As pointed out by Gordon, the MDW satellites should be subject to the following relation:

$$Q \approx (8\pi/c_0^2) (m/\sqrt{3}) (1 + m/8) \quad [1]$$

where Q is the wavevector of the satellites, m the misfit and c_0^2 the lattice constant of the related Xe-layer. For not too large misfits, these MDW satellites should appear in the same direction as the principal reciprocal lattice vector of the Xe-layer, i.e. in the $\vec{\Gamma}\bar{M}_x$ -direction. On the other hand, the commensurate buckling, if present, has its maximum amplitude in the $\vec{\Gamma}\bar{K}_x$ -direction, i.e. in the direction of close packed Xe-rows. Moreover, these commensurate buckling satellites should only be present for orientations where a high order commensurability becomes favorable, i.e. in the present case at monolayer completion ($m = 9.6\%$) (see ref. 12), whereas the MDW satellites should be present in the entire misfit range where the Xe-layer is rotated (7.2%-9.6%).

In fig. 3a we show polar He-diffraction scans in the vicinity of the specular beam, with the scattering plane oriented along the $\vec{\Gamma}\bar{M}_x$ -direction, for rotated Xe-layers of misfit 7.8% and 8.3%, respectively. In both scans satellite peaks are obvious. The dispersion of these peaks is shown in fig. 3b, and compared with Gordons prediction for the MDW given above. The data follow qualitatively the predicted dependency: the agreement becomes quantitative at misfits larger than $\approx 8\%$. The reason for the better agreement at large misfits can be understood upon inspection of the lower part of fig. 3b, where the variation of the rotation angle φ versus misfit m for Xe/Pt(111) is shown. The Novaco-McTague model calculations as well as Gordons analysis of the MDW have

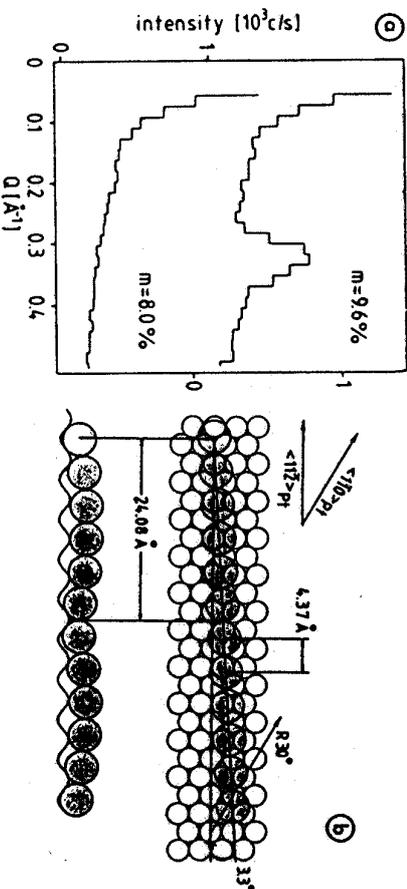


Fig. 4: a) Polar He-diffraction scans of rotated Xe-monolayers on Pt(111) in the vicinity of the specular peak ($Q = 0\text{\AA}^{-1}$) taken along the $\vec{\Gamma}\bar{K}_x$ -azimuth, at $m = 8\%$ and 9.6% , respectively. b) Upper and side view of a 3×3 rotated domain of the complete monolayer. The Xe domain is represented schematically by a chain of twelve atoms.

been performed in the linear response approximation of the adsorbate-substrate interaction. This approximation is only justified at larger misfits (see also ref.13). Indeed, the φ versus m data substantially deviate from the NM-curve for misfits less than $\approx 8\%$. The measured intensities of the MDW satellites vary between 10^{-2} of the strongest Xe layer diffraction peak at small misfits to about 10^{-1} at large misfits. These intensities can be correlated with the amplitudes of the MDW. By means of eq.6-8 in ref.9 and by using realistic values for the Xe/Pt(111) potential (as listed in ref.14) amplitudes of the order 0.1\AA are obtained.

In fig.4 we show scans like in fig.3a but measured in the $\bar{\Gamma}K_x$ -direction for rotated Xe-layers of misfits 8% and 9.6% (monolayer completion). At variance with the scans in the $\bar{\Gamma}M_x$ -direction (fig.3a), a satellite peak is observed only for the complete Xe monolayer ($m = 9.6\%$). The location of this satellite peak at $Q = 0.315\text{\AA}^{-1}$ corresponds to a buckling period of 23\AA and can be ascribed to a high order commensurate structure shown in fig.4b and described in detail in ref.12. Being present only at a particular misfit this peak does not originate from a MDW. Thus, only at monolayer completion the rotated Xe-layer locks-in on the substrate, and both MDW satellites in the $\bar{\Gamma}M_x$ -direction, as well as commensurate buckling satellites in the $\bar{\Gamma}K_x$ -direction are observed; at other misfits only MDW satellites are present.

We have given here a few examples from the fascinating variety of phases of physisorbed films uncovered by high resolution He-scattering. Note that all have been obtained on a close packed, very smooth metallic substrates. As stated in the introduction, these various modulated adlayer structures arise from the competing interactions which favor different periodicities: the "natural" lattice constant of the adlayer and the substrate potential. The existence of these phases implies that the strength of the corrugation of the holding potential of the very "smooth" Pt(111) substrate and of the rare gas atom lateral potential are of the same order. This contradicts the idea of almost perfect "smoothness" of the close packed metal surfaces experienced by rare gases

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