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SYMMETRY BREAKING COMMENSURATE-INCOMMENSURATE TRANSITION OF MONOLAYER Xe PHYSISORBED ON Pt(111)

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We report a high resolution He-diffraction study of the commensurate- incommensurate transition of monolayer xenon physisorbed on Pt(111). The experimental results show that we have been able to observe for the first time a $(\sqrt{3}x\sqrt{3})R30°$ commensurate (C) to striped incommensurate (SI) transition. The striped domain walls are found to run into the $\overline{\Gamma K}$-direction, i.e. the uniaxial compression is in the $\overline{\Gamma M}$-direction. The C-SI transition appears to be continuous within the experimental accuracy and the incommensurability in the weakly incommensurate phase follows a 1/2 power law versus reduced temperature.

Detailed investigations of two-dimensional CI-transitions have been performed theoretically [1], experimentally [2] and by computer simulations [3]. By generalizing the one dimensional Frank-Van der Merwe model, it has been assumed that, close to the CI-transition, the I-phase can be considered as a regular array of domain walls, separating commensurate domains [1]. Depending on the energetics of the wall intersections [1], these domain walls may either form a striped phase corresponding to a uniaxially compressed-phase (SI) or a hexagonal (HI) honeycomb network, corresponding to a uniform compression. Bak, Mukamel, Villain and Wentowska (BMVW) pointed out [4] that the CI-transition has to be of second order if the hexagonal symmetry is broken, i.e. if a striped phase (SI) is formed. On the other hand, if the hexagonal symmetry is preserved, a first order transition from the commensurate to the incommensurate (HI) phase should occur. The experimental confirmation of this prediction is still controversial. The most intensively studied experimental system, Kr/graphite (Gr) [2] shows, at variance with the BMVW theory, a continuous transition while hexagonal symmetry is preserved. Recently Villain and Gordon [5] argued that impurity effects might be responsible for the quenching of the striped phase in the CI-transition of Kr/Gr.

The system Xe/Pt(111) appears to be a good candidate for a model system to investigate the properties of 2D-physisorbed phases and their mutual transitions. Similar to the Kr/Gr system, considered so far as the model system, a Xe monolayer on Pt(111) has been shown to exhibit the following main phases [6]: a commensurate $(\sqrt{3}x\sqrt{3})R30°$-phase (C), an incommensurate-phase (I) and an "incommensurate" rotated phase (R), which -when fully developed- consists of an equal number of domains rotated $\pm 3.3°$ with respect to the R30° direction. The Pt(111) surface certainly has the advantage that it can be brought near to the requirements of an ideal, periodic substrate; its mosaic structure is negligible and by refined preparation procedures the amount of defects and impurities can be reduced below 0.1% [7]. This might be the reason why the CI-transition induced by anharmonic effects when varying the temperature at constant coverage and which has been predicted to take place around 34K for Kr/Gr [8] (with the transition temperature only slightly varying with chemical potential, i.e. with coverage) but not yet observed [9] has been found to exist indeed for Xe/Pt(111) around 60K [6]. In this paper we report a high resolution helium diffraction study of the commensurate-incommensurate (CI) transition of monolayer xenon physisorbed on Pt(111). We show that the commensurate (C) phase transforms to a *striped incommensurate* (SI) phase in the initial stage of the transition. This symmetry breaking transition is found to be continuous within the experimental accuracy.

The experiments presented here have been performed in the UHV high resolution He-scattering apparatus described in detail elsewhere [10]; the relevant features are the following. The He-beam generator and the detector being immobile, the total scattering angle is fixed, $\theta_i + \theta_f = 90°$. The angular divergence of the incident beam and the angle subtended by the detector ionizer opening are both equal to 0.2°. The energy of the incident He-beam in the experiments reported here is 17.4meV at an energy spread of $\Delta E \approx 0.25$meV. The base pressure is in the low 10^{-11} mbar in order to keep the well prepared Pt(111) surface (< 0.1% defects and impurities) as well as the Xe layers free of impurities. The average terrace width of the Pt(111) surface is about 3000A. The symmetry directions will be noted in the following with respect to the orientation of the commensurate Xe-layer.

The CI-transition of Xe on Pt(111) has been investigated as a function of various parameters: of surface temperature at constant Xe-coverage, of Xe-coverage and of 3D-Xe equilibrium pressure at constant temperature. The observed microscopical behaviour during the CI-transition being in all these cases the same, we will confine here to the CI-transition induced by varying the temperature at constant Xe-coverage $\Theta = 0.30$ ($\Theta = 1$ corresponds to $1.5x10^{15}$ Xe atoms per cm^2). The same behaviour is observed in the whole range $\Theta < 0.33$. Xe was adsorbed from the gas phase at pressures around 10^{-8} mbar; when the desired coverage was reached, the 3D-Xe gas was pumped off.

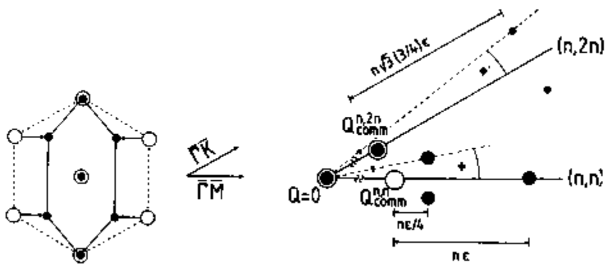

Fig.1. Real and reciprocal lattice of the commensurate Xe overlayer on Pt(111) and of the Xe layer upon uniaxial compression in the $\overline{\Gamma M}$-direction (o) denote the $\sqrt{3}x\sqrt{3}$ commensurate and (•) the uniaxial compressed incommensurate structure.

Before discussing the experimental results in detail, let us have a look at the diffraction pattern expected from a striped uniaxially compressed phase adsorbed on a single crystal substrate. The schematic structure of the commensurate $\sqrt{3}x\sqrt{3}$ (o) and of a striped incommensurate phase (•),uniaxially compressed in the $\overline{\Gamma M}$-direction, is shown in real space on the left side of fig.1. The corresponding diffraction patterns for the (n,n) and (n,2n) diffraction orders are shown on the right side of fig.1. These patterns have been obtained for striped domains assuming that the striped phase is fully relaxed, i.e. is an uniaxially compressed phase, and of course that the symmetry directions are threefold degenerated [11]. The (n,n) order pattern consists of an out of plane doublet located at $Q^{n,n}_{comm} + n\varepsilon/4$, symmetrical with respect to the $\overline{\Gamma M}$-direction, and one peak located in the $\overline{\Gamma M}$-direction at $Q^{n,n}_{comm} + n\varepsilon$. The (n,2n) pattern consists of a peak at the commensurate position $Q^{n,2n}_{comm}$ in the $\overline{\Gamma K}$- direction and a weak out of plane doublet at $Q^{n,2n}_{comm} + n(3/4)\varepsilon\sqrt{3}$ [12]. A hexagonal domain wall network (uniform compression) leads to quite different diffraction patterns (for details see for example ref.13). Thus, uniaxial and uniform compression are distinguishable and in the former case the direction of the compression can be determined.

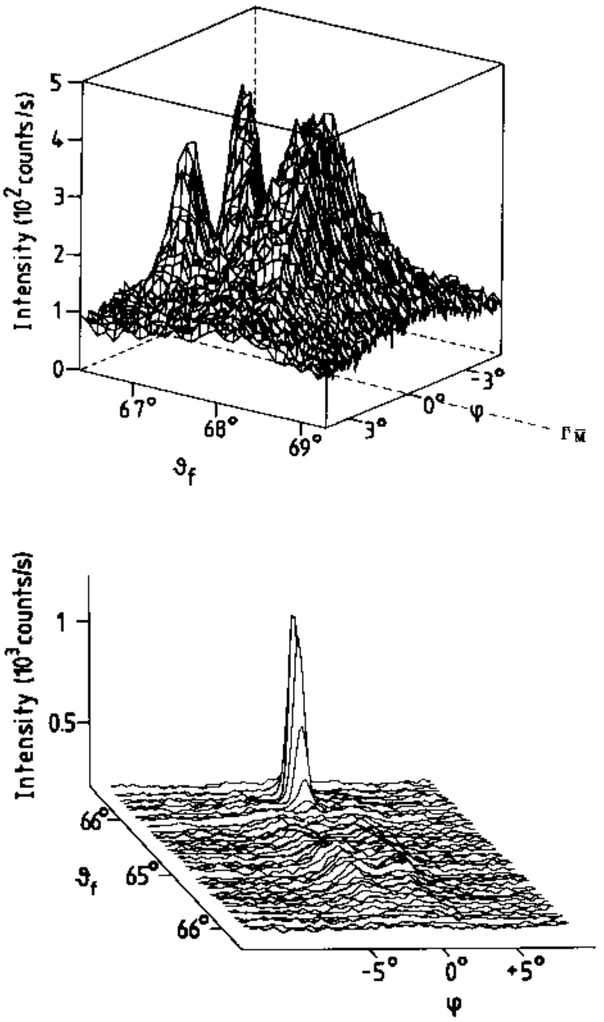

Fig.2. 3D-diffraction plot of the a) $(2,2)_X$, and b) $(1,2)_X$, diffraction features at 54K. θ_f denotes the polar angle, while φ the azimuthal angle with respect to the $\overline{\Gamma M}$ and $\overline{\Gamma K}$-directions, respectively.

We discuss first the basic crystallography of the incommensurate phase as deduced from the measured patterns. Fig.2 gives an overview of the $(2,2)_X$, and $(1,2)_X$, diffraction features obtained from a Xe layer of coverage $\Theta \simeq 0.30$ during the CI-transition at 54K. The plots have been obtained by monitoring series of azimuthal scans (i.e. constant Q scans in the reciprocal space). The comparison with fig 1. shows that the incommensurate xenon layer on Pt(111) is a striped phase (SI) with a uniaxial compression in the $\overline{\Gamma M}$-direction. Indeed, a three-peak structure for the $(2,2)_X$, diffraction feature, with the doublet located at $Q^{2,2}_{comm} + 0.048 A^{-1}$ and the single peak located at $Q^{2,2}_{comm} + 0.190 A^{-1}$ is observed (with $Q^{2,2}_{comm} = 3.02 A^{-1}$); whereas the $(1,2)_X$, pattern consists of a single peak at the commensurate position and a shallow doublet with the maximum intensity at about $Q^{1,2}_{comm} + 0.13 A^{-1}$ (with $Q^{1,2}_{comm} = 2.62 A^{-1}$). The observed incommensurability deduced from the well defined polar location of the peaks in fig. 2a is $\varepsilon = 0.95$A and corresponds to an interrow distance in the $\overline{\Gamma M}$-direction of $d_{SI} = 3.91 A$. This results in a misfit $m = 1 - d_{SI}/d_C = 0.059$, where $d_C = 4.80 x \cos 30°$ A is the interrow distance of the commensurate Xe-structure in the same direction. From the measured polar and azimuthal peak widths in fig.2 we can also estimate average domain sizes of the incommensurate layer. For the $\overline{\Gamma K}$-direction, i.e. parallel to the walls, we obtain ~350A and for the perpendicular $\overline{\Gamma M}$ -direction ~50A.

The analysis in the last paragraph has shown that the incommensurate Xe-layer on Pt(111) at misfits of about 5% is a striped phase with the domain walls strongly relaxed, i.e. a uniaxially compressed layer. Indeed, for less relaxed domain walls, depending on the extent of the wall relaxation and on the nature of the walls (light, heavy or superheavy [14]) additional satellites in the (n,n) diffraction patterns should appear [15]. In the case of a weakly incommensurate layer (misfits below ~3%) we observe an additional on axis peak at $Q^{2,2}_{comm} + \varepsilon/2$ in the (2,2) diffraction pattern. In order to determine the nature of the domain walls we have calculated the structure factor for the different domain wall types as a function of the domain wall relaxation following the analysis of Stephens et al. [13]. Detailed results of this analysis will be reported elsewhere [16], here we note only that the observed additional on axis satellite at $Q^{2,2}_{comm} + \varepsilon/2$ in the weakly incommensurate phase is consistent with the occurence of supeheavy striped domain walls [17], and that the observed peak intensities can be reproduced with a domain wall width of $\lambda \approx 4$-5 Xe interrow distances.

Let us now discuss in some detail the behaviour during the CI-transition. Figure 3 shows polar scans of the $(2,2)_X$, diffraction features taken along the $\overline{\Gamma M}$-direction at various temperatures. At the highest temperature, 73K, far away from the CI-transition, a very sharp diffraction peak is observed at $\theta_f = 66.7°(Q^{2,2}_{comm} = 3.02 A^{-1})$, which corresponds to a lattice parameter of 4.80 ± 0.03A, obviously characterizing a $(\sqrt{3}x\sqrt{3})R30°$ commensurate structure. The average domain size determined from the peak width is ~800A. As the temperature is decreased the Xe-layer undergoes the C-SI transition, and the striped phase develops in a continuous way. Note,that the "on axis" satellite at $Q^{2,2}_{comm} + \varepsilon/2$ of the superheavy domain walls can only be detected in the weakly incommensurate phase. With increasing incommensurability the wall relaxation strongly increases. The measured diffraction patterns suggest a continuous phase transition; a small but not resolved discontinuity cannot be excluded definitely. However, the continuous character of the C-SI transition goes along well with the perfect reversible temperature behaviour, already noted in [4] for the gros features of the transition, and confirmed in the present experiment for all details.

The measured misfit m in the striped phase varies in the measured data from 1.6% to 6.5%. The smallest incommensurability we have been able to detect corresponds to a domain wall separation of about 60 interrow distances, i.e. is ~250A. Figure 4 shows the average misfit of the striped phase in the $\overline{\Gamma M}$ -direction versus reduced temperature, deduced from diffraction scans like those in fig.2+3 [18].

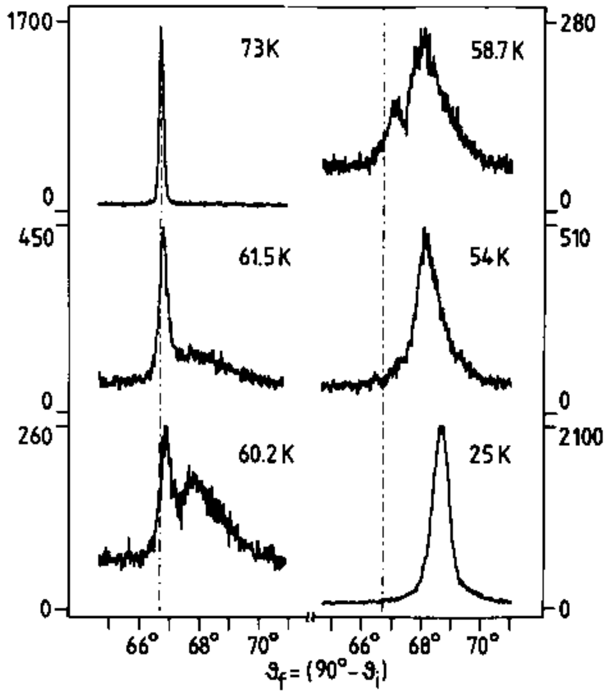

Fig.3. Polar scans of the $(2,2)_{M}$ diffraction feature at various temperatures during the CI-transition at constant coverage Θ≈0.3. All scans are taken along the $\overline{\Gamma M}$-direction.

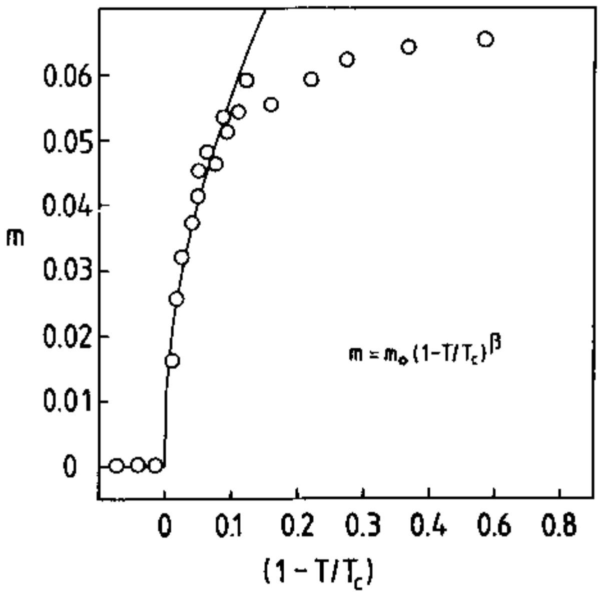

Fig.4. $\overline{\Gamma M}$-uniaxial misfit m vs reduced temperature. The solid line represents the power law fit.

Pokrovsky and Talapov have studied the effect of the temperature in the case of parallel domain walls and found that the domain wall density in the weakly incommensurate regime, i.e. the misfit m, should obey a power law $m \sim (1 - T/T_c)^{1/2}$ [19]. Parallel domain wall phases and the 1/2 power law dependence of the misfit have been observed in anisotropic systems, like Xe/Cu(110) [20] or bromine intercalated graphite [21]. The Pokrovsky-Talapov model may essentially be applied to a substrate of uniaxial symmetry [22], although the original model calculations [19] are performed for an isotropic substrate. In fig.4 we have analyzed the data in the low misfit range with a least-squares fit of a power law form. We have performed the fit by using the data points only up to 4.8% in accordance with Erbil et al. [21] who have found the β = 1/2 power law to be valid only for misfits less than 4-5% in the case of bromine intercalated graphite. At large misfits, i.e. at higher domain wall densities, the repulsive interaction between domain walls hinders the creation of new walls, and thus leads to deviations from the Pokrovsky-Talapov prediction. The solid line in fig.4 is a least-squares fit of a power law form $m = m_o(1 - T/T_c)^{\beta}$; the best fit parameters are $T_c = 61.7K$, $m_o = 0.18$, and $\beta = 0.51 \pm 0.04$. The exponent $\beta = 0.51$ is in good agreement with the Pokrovsky-Talapov prediction [19].

Finally, we note that upon coverage increase the striped phase (SI) transforms to a hexagonal incommensurate phase (HI) at misfits ≥ 6.6%. The HI-phase displays a continous transition from an R30° to a rotated R30° ± 3.3° orientation upon further increase of the average misfit. This transition is currently under investigation and will be presented in a later report.

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11. In the calculation of the diffraction patterns in fig.1 we have assumed rectangular domains with the length in the $\overline{\Gamma K}$ direction 7 times larger than in the $\overline{\Gamma M}$ direction. The assumption was made because the peak profile analysis (see below) shows that the corresponding correlation lengths are in a similar ratio.

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