Pokrovsky-Talapov commensurate-incommensurate transition in the CO/Pd(100) system

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X-ray-diffraction measurements have been carried out for a monolayer of CO on the Pd(100) surface. Because of equilibrium with the gas phase, at constant pressure a series of structures is formed with varying temperature (varying coverage). One structure at 350 K selected for crystallographic analysis, is found to be a commensurate lattice with $p2gg$ symmetry of CO molecules bound in substrate-bridge sites. The vibration amplitudes of the molecules are substantially larger in-plane than out-of-plane. Upon cooling, a phase transition is crossed beyond which the structure becomes incommensurate. Symmetry considerations and the measured exponent of 0.5 ± 0.05 establish this transition to be in the Pokrovsky-Talapov universality class. [S0163-1829(96)01444-0]

Adsorbate layers provide an extensive playground for the test of theoretical predictions for two-dimensional phase transitions. These systems are important from the theoretical point of view because they are intermediate between the one-dimensional and three-dimensional worlds. In one dimension (in systems with short-range forces of finitely many-body character) no phase transition occurs,[1] while in three dimensions the symmetry-based Landau theory very often predicts the essentials of the phase transitions. In two dimensions these symmetry arguments often fail because of the strong fluctuations of the order parameter Φ, i.e., terms of $\langle\Phi^2\rangle$, which are neglected in the Landau approach.[2] Another unique characteristic of two-dimensional systems for the study of phase transitions is the theoretical possibility of *algebraic* decay of correlations expected for a floating solid phase; this special state of matter, existing only in two dimensions, lies between the widespread extremes of long-range (solidlike) order and exponentially decaying (liquid-like) correlations.[3,4] In experimental systems comprising adsorbates bound to well-ordered substrates, commensurate structures frequently occur, because of the preference of the adsorbate for well-defined adsorption sites. Then the symmetry group of the adlayer is in general a subgroup of that of the substrate, the solid phase is represented by a commensurate adlayer structure. The floating solid phase is incommensurate with the substrate, which in the general sense means that it can be continuously shifted over the substrate lattice without any cost of energy and hence has continuous translational symmetry.

In lattice gas systems very often domain-wall phases occur, made up of regions of locally commensurate structures separated by domain walls. Depending on the adlayer-substrate misfit different kinds of walls can be differentiated with different free energies, for example, ''heavy'' and ''light'' walls containing additional molecules or vacancies, respectively. The energetic preference for one kind of domain wall over an other will then introduce a ''chirality'' to the system. This in general leads to well-defined sequences of the commensurate domains and hence to incommensurate structures. The commensurate-incommensurate transition (CIT) is one of these phenomena, where the commensurate phase undergoes a transition into an incommensurate floating solid. The counterpart is a chiral melting transition, where the commensurate phase melts into an incommensurate fluid phase.[5] In the present paper we report on the phase transition behavior of the $(2\sqrt{2}\times\sqrt{2})$ phase formed by CO on the Pd(100) surface. This commensurate phase undergoes a CIT upon variation of the temperature, which was studied by x-ray diffraction. Since the change of commensurability is coupled with a change of coverage, this was accommodated by equilibration with the CO vapor phase.

A theoretical foundation of incommensurate structures has existed for some time through the one-dimensional van der Merwe energy-minimization model for the stable state of interacting balls in a periodic potential, which leads to a soliton description of the equilibrium structure. The solitons correspond to domain walls which divide regions of commensurate structure. Depending on the relative strengths of the interactions and the substrate potential, the domain walls can be either sharp or broad. In a diffraction experiment, the sharpness of the domain walls results in a lesser or greater number of satellite reflections, and so it can be determined reliably.

A well-known theory of CIT's has been laid down by Pokrovsky and Talapov.[6,7] The domain walls of the incommensurate phase are energetically unfavorable to the pure commensurate regions, but also fluctuate entropically and thereby interact with each other. In thermodynamic equilibrium, the density of domain walls therefore varies with temperature and vanishes at a critical temperature T_{CIT}. The incommensurability, or density of domain walls, varies as a power of the reduced temperature, with an exponent of 0.5. The stability of the incommensurate phase is determined by the degeneracy of the sublattice p, which is the number of independent positions on the substrate that the overlayer atoms can occupy. When $p>2$ the incommensurate floating phase becomes stable in the vicinity of the commensurate phase. For degeneracies $p>3$ the commensurate phase is expected to undergo a CIT for all chiralities (Ref. 4 and references therein). The commensurate phase and the liquid phase are believed to meet at most in one (tricritical) point.

Numerous examples of such transitions have been studied in the past, starting with the adsorption of noble gas adlayers on graphite[8,9] and on other surfaces.[10] However, many of these systems exhibit hexagonal symmetry, complicating the phase diagram because of domain wall crossings.[11,12] Uniaxial CIT's have been observed, for example, for Xe/Cu (110),[13] bromine-intercalated graphite,[14,15] and Xe/Pt(111).[16] Chemisorbed systems are very often governed by sharp domain walls;[17,18] however, it is often impossible to control the chemical potential, which renders a direct comparison between theory and experiment rather difficult. In the recent past, a different mechanism of a CIT via domain wall evaporation has been discussed for several chemisorbed systems like Ba/Mo(110), Te/Mo(110), and S/Ru(0001),[19] which under certain circumstances renders the transition first order. Chiral transitions have been observed for the $p=3$ case for Si(113) (Refs. 20–22) and Ge(113).[21]

In the present paper we study the evolution of the commensurate $(2\sqrt{2}\times\sqrt{2})$ structure of CO/Pd(100) with the substrate temperature. The surface system is in equilibrium with the gas phase, hence maintaining a reservoir with constant chemical potential. (The difference between the sample and the gas temperature introduces a small kinematical correction, which can be neglected in the present case.[23]) Low-energy electron diffraction (LEED) experiments on CO/Pd(100) have detected a continuous variation of the lattice constant with temperature.[24] In these early studies the overlayer was thought to compress uniformly upon decreasing the temperature, due to increasing CO coverage on the surface. Later, a structural model was proposed, based on a commensurate centered $(2\sqrt{2}\times\sqrt{2})$ overlayer structure, in which heavy domain walls are introduced to accommodate additional CO.[25,26] We report an x-ray-diffraction study of the CO/Pd(100) system in which we measured the variation of the overlayer lattice constant with temperature at a number of different CO pressures. In each case we found good agreement with the exponent predicted by the Pokrovsky-Talapov theory. We also measured the structure of the commensurate phase, which agreed with the previous LEED study. We evaluated the anisotropic thermal-vibration amplitudes, and found a large value parallel to the surface, as expected for the weakly directional bonding of CO with the metal substrate.

The experiments were carried out at beamline ID3 of the European Synchrotron Radiation Facility (ESRF). ID3 is a dedicated facility for surface x-ray diffraction.[27] A Pd(100) substrate was prepared by sputtering and annealing at 700 °C. The crystal surface was optically aligned on the omega axis of the diffractometer using a laser, and the crystal lattice was aligned using its bulk {111} Bragg peaks. The bulk cubic Miller index system was used to map reciprocal space throughout with (001) perpendicular to the surface. In this way the miscut was determined to be 2.6° approximately running along the (010) azimuth. CO was introduced to the vacuum chamber by means of a leak valve, and the measurements were carried out in the presence of the gas. The sample temperature was measured by means of a PT100 resistor.

When $p_{CO}=10^{-7}$ mbar, the commensurate overlayer structure was present only within a temperature range 340 <T<355 K, as evidenced by superstructure diffraction peaks at (1,0.5,0.1) and (0,1,0.1). These correspond to the unit cell of the $(2\sqrt{2}\times\sqrt{2})$ structure identified by Tracy and Palmberg.[24] No peaks were detected at (0.5,1,0.1) or (1,0,0.1) indicating that only a single domain of the superstructure had formed, presumably stabilized by the steps which are present due to the strong surface miscut. The intensity of the peaks was rather low, around 300 counts/s, substantially weaker than the 2000 counts/s previously seen from a CO monolayer on Ni(110) at the same beamline.[28]

We measured a set of x-ray structure factors to identify this phase. We determined the integrated intensity of omega scans with background subtraction and corrected for the Lorentz-polarization factor and sample area appropriate for the diffractometer geometry. Very few reflections beyond the innermost orders had much intensity, suggesting large Debye-Waller factors, as seen before for CO structures.[28] The reproducibility of symmetry equivalent reflections was only 17%. We first found that all reflections with indices $(0,k/2,L)$ for k integer and $(h,0,L)$ for h odd were absent, which indicates either a centered unit cell, or else two perpendicular glide-line symmetry axes, as featured in the $p2gg$ plane group. The first superstructure reflection of the class $(h,k/2,L)$, which would be sensitive to the difference between these symmetries, was at such large angle to be indistinguishable from zero. Therefore, we could not fully determine the plane group crystallographically.

The structure we determined from analysis of these data is the same as that proposed by Tracy and Palmberg[24] and confirmed by LEED analysis by Behm *et al.*[29] It is shown in Fig. 1(a). The two CO molecules per unit cell sit in substrate bridge sites and provide a center of symmetry, but this is also consistent with the plane group $p2gg$. In accordance with Biberian and Hove[25] we consider the correct classification to be $p2gg(2\sqrt{2}\times\sqrt{2})$ because $c(2\sqrt{2}\times\sqrt{2})$ cannot describe the symmetry of the substrate as well. We also identify the bridge site as the only possibility compatible with either plane group, and hence with the systematic absences, as shown in Fig. 1.

The agreement between the calculated and observed structure factors is shown for two rods in Fig. 2. With such high symmetry in the structure, the only degrees of freedom are the CO bond length and the Debye-Waller factors of the C and O atoms, but even these were too many to be deter-
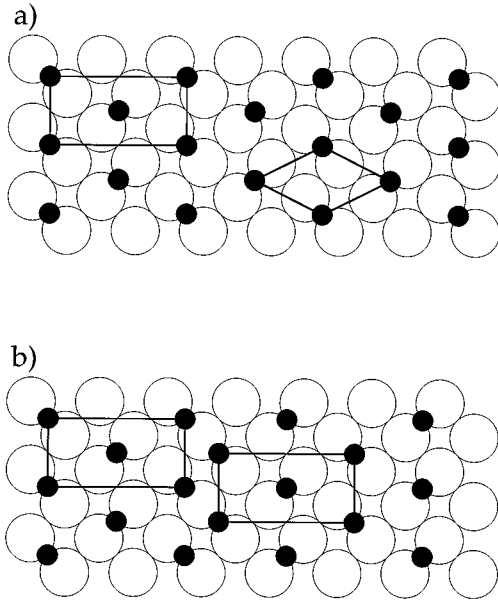
a)

b)

FIG. 1. (a) Structural model of the $(2\sqrt{2}\times\sqrt{2})$ CO/Pd(100) structure as proposed first by Tracy and Palmberg (Ref. 24). A $p2gg(2\sqrt{2}\times\sqrt{2})$ unit cell and the primitive unit cell are indicated. (b) structural model of a dense-domain wall, separating two $(2\sqrt{2}\times\sqrt{2})$ domains (large open circles, Pd substrate; small filled circles, CO molecules).

mined reliably by the limited data. The CO bondlength was found to be 1.3 ± 0.2 Å, and the best parametrization of the Debye-Waller factors was $B_{XY}=16\pm5$ Å^2 parallel to the surface plane and $B_Z=4\pm8$ Å^2 perpendicular. These large values explained both the drop of intensity along the reciprocal lattice rods, seen in Fig. 2, and the very strong drop off with increasing diffraction order in-plane. The corresponding vibration amplitudes are $\sqrt{\langle u_{XY}^2\rangle}=0.45\pm0.07$ Å and $\sqrt{\langle u_Z^2\rangle}=0.2\pm0.2$ Å. The structure gave an agreement of $\chi^2=2.3$ for three parameters and 30 independent data. No crystal truncation rod (CTR) data were included in the final fit because
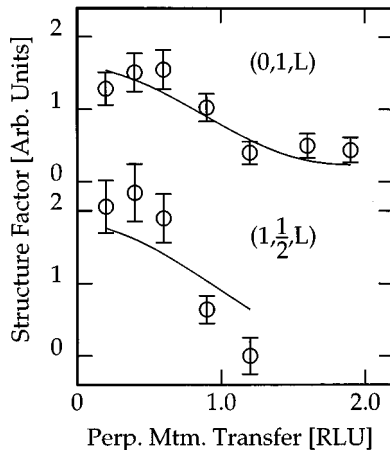

FIG. 2. Structure factors versus perpendicular momentum transfer L (in reciprocal lattice units) for the $(0,1,L)$ and the $(1,1/2,L)$ rods (symbols, measured structure factors; lines, calculated structure factors).
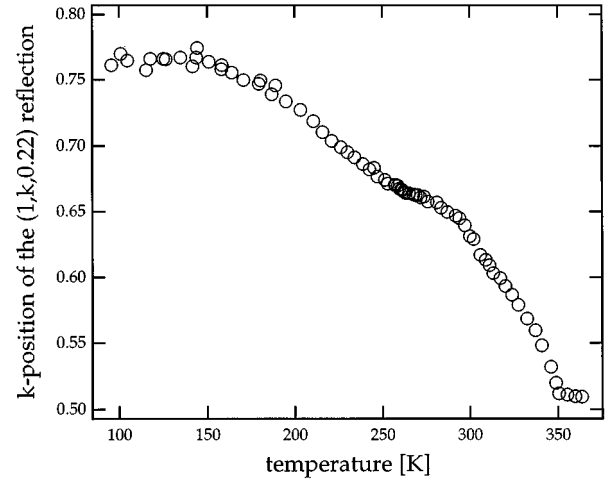

FIG. 3. k position of the $(1,k,0.22)$ peak as a function of temperature. Above 340 K the peak corresponds to the $(2\sqrt{2}\times\sqrt{2})$ structure. For the slight offset of $\Delta k\approx0.01$ see discussion in the text.

they were found to be hardly sensitive to the structure, partly because C and O atoms are so much lighter than Pd. Also, because of the symmetry, there is no contribution of the CO to the $(1,1,L)$ CTR, and the Debye-Waller effect is already large at the $(2,0,L)$.

In Fig. 3 we present the evolution of the (commensurate) $(1, 0.5, .22)$ peak with temperature at $p_{CO}=1.3\times10^{-7}$ mbar. The $(2\sqrt{2}\times\sqrt{2})$ superstructure is stable only between 350 K and 365 K. Above 365 K the superstructure peak vanishes and broadens continuously, suggesting a continuous melting transition from the commensurate solid phase into a liquid phase. Because of the already weak peak intensity in the commensurate region we could not follow this transition in detail. However, from the fourfold degeneracy of the $(2\sqrt{2}\times\sqrt{2})$ domains this transition is expected to lie in the universality class of the four-state Potts model. The lock-in position of the commensurate phase is not exactly at $k=0.5$, as it was expected for an infinitely wide $(2\sqrt{2}\times\sqrt{2})$. Its k value is increased by $\Delta k\approx0.01$, which we interpret to be caused by intrinsic antiphase domain boundaries, imposed on the structure by the finite terrace size. The shift of the peak is compatible with a domain size of the commensurate structure of ≈200 Å, as derived from the peak width. The average terrace width, as determined from the miscut of 2.6° is ≈43 Å. The observed domain sizes of about 200 Å hence indicate significant step bunching.

Below 350 K the peak starts shifting from the commensurate position. The tangent to the curve upon the starting of the peak shift is about vertical, defining a sharp transition into the incommensurate phase. Decreasing the temperature further leads to a gradual shift of the peak up to $k=0.76$ without any abrupt change of the slope. We can form a partial description of the incommensurate phase because we observed small satellite diffraction peaks. The degree to which satellite reflections are observed is related to the sharpness of the domain walls in the soliton description above. There are two extreme limits: a uniformly compressed incommensurate structure has, in effect, very wide domain walls and gives no satellite reflections; the other limit, which has perfect abrupt domain walls separating ideal commensurate regions has
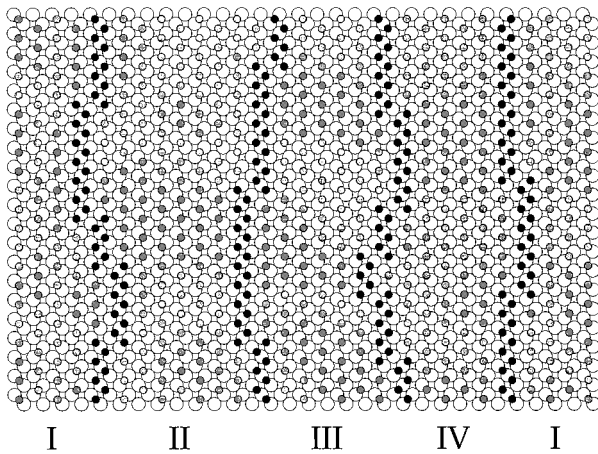
FIG. 4. Sketch of the incommensurate floating solid, where the commensurate domains of the $(2\sqrt{2}\times\sqrt{2})$ structure are separated by single, dense domain walls. The four translational domains are indicated.

many satellites. The intensity of these satellites is modulated by the slit function and hence the intensity of further out satellites decreases very rapidly. The expected diffraction pattern was worked out in detail by Kortan *et al.*, Mochrie *et al.*,[14,15] and Zeppenfeld *et al.*[30] From the (small) satellites observed in our measurements it follows that the domain-wall picture is indeed appropriate to describe the incommensurate phase, although no details on the apparent width of the domain walls could be derived. This is in accordance with the interpretation of previous LEED data by Berndt and Bradshaw.[26] However, due to multiple scattering LEED cannot easily distinguish between these two descriptions of the incommensurate phase.

In the vicinity of the commensurate phase, Berndt and Bradshaw assumed densely packed, single domain walls, separating the commensurate domains [Fig. 1(b)]. Compared with double-domain walls, such domain walls exhibit a lower local density of CO molecules. Considering slight mutual repulsion among neighboring CO molecules, as follows from the behavior of the adsorption energy with coverage,[24] single-domain walls should be preferred over double ones. A typical situation of the domain-wall phase is depicted in Fig. 4. Further lowering the temperature or increasing the coverage, respectively, leads to the formation of more and more domain walls, finally ending up in a high-density phase, where the peak is found at $k\approx0.76$. We do not detect any hint for a further phase transition, besides that at 350 K. In particular the $(4\sqrt{2}\times\sqrt{2})$ phase,[26] which is crossed at $k=0.75$, rather seems to be a compression phase, formed from the incommensurate phase by increasing the number of domain walls and hence finally becomes ''accidentally'' commensurate. We did not observe strong indications for a locking-in of the incommensurate structure at higher-order commensurate positions. However, the curve shows a slight dip close to $k=0.66$, which could be interpreted as indicating a tendency towards stabilization of the commensurate $(3\sqrt{2}\times\sqrt{2})$, which consists of alternating $(2\sqrt{2}\times\sqrt{2})$ structures and dense domain walls. This structure represents the densest structure, formed by single-domain walls, before introducing double domain walls. Indeed, infrared absorption data show a sharp-
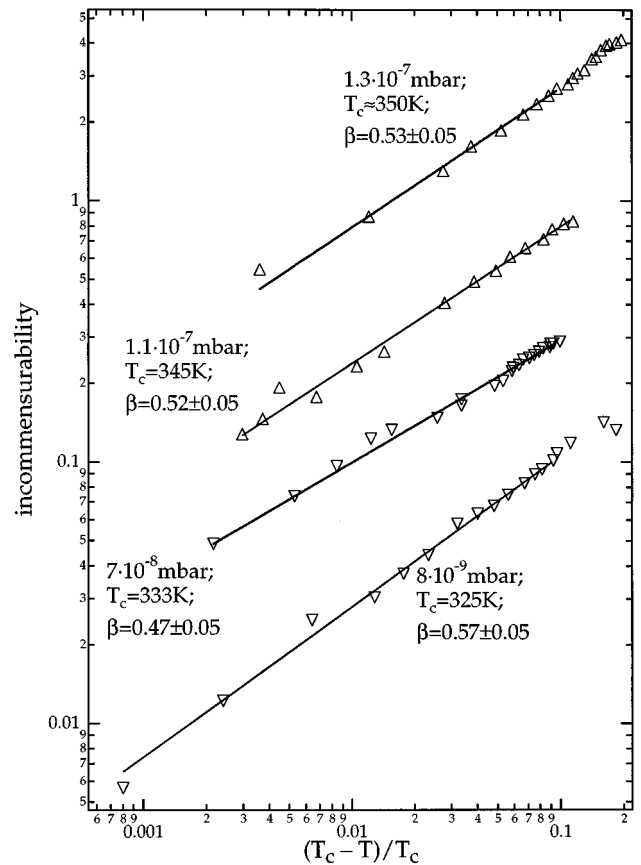

FIG. 5. Incommensurability versus reduced temperature for four different CO pressures. Pressures, reduced temperature, and fitted exponent are given. Upward and downward triangles correspond to ramping up or down of the temperature during the experiment, respectively. The curves are shifted by factors of 3 on the vertical axis for clarity. The absolute value of the critical temperature for the uppermost curve is only approximate, because in this experiment a temperature gradient between sample and the PT100 resistor was introduced by the use of a cryostat.

ening of the adsorption features near commensurate positions indicating increasing order.[31]

Allowing for only one kind of domain wall, as seems to be appropriate in the vicinity of the $(2\sqrt{2}\times\sqrt{2})$, leads to a regular sequence of the four translational domains of the $(2\sqrt{2}\times\sqrt{2})$ (Fig. 4). Hence, correlation along the incommensurate direction is maintained. However, at finite temperature these walls are expected to show thermal excitations, as illustrated by the kinks in Fig. 4, which lead to the wiggling appearance of the pattern, partly destroying the long-range order and leading to an algebraic decay of the correlation,[4] which is characteristic of an incommensurate solid phase. The formation of domain walls might compete with the formation of dislocations, which eventually destroys the long-range order and leads to a liquidlike phase. As mentioned above, it is expected on theoretical grounds that for $p>3$, only a direct transition from the commensurate phase into an incommensurate solid should be possible. Indeed, in the present case $p=4$. Only at higher incommensurabilities a (second) melting transition from the incommensurate solid into an incommensurate fluid becomes possible. However,

we found no indications for such a melting transition.

To classify the transition in the usual way, we determined its critical exponent. Figure 5 shows a log-log plot of the incommensurability $(k-k_0)$ versus the reduced temperature $(T_c\text{-}T)/T_c$ for four different pressures (the four curves are shifted with respect to each other by factors of 3). The critical temperature corresponds to the beginning of the shift of the incommensurability and was used as an input to the fit. The fitted exponents agree within the error with 0.5, irrespective of whether the temperature was ramped up or down. The error bars of the exponents are derived from the uncertainties in the determination of the critical temperature and the standard deviation of the fit. This value of 0.5 is in perfect agreement with the theoretical expectation, according to which a continuous transition of a $p=4$ phase should exhibit Pokrovsky-Talapov behavior, signaling a transition from the commensurate phase into an incommensurate floating solid. This gains further support from the fact that the peak width, or the inverse of the correlation length, shows no detectable change close to the transition. Theoretically, there is a clear distinction between a chiral melting transition and a CIT.[5] As for a chiral transition, both the correlation length and the wall separation go to infinity, the ratio of peak width and incommensurability reaches a constant $\neq 0$. For the CIT mainly the peak shape and not the width changes at the transition, indicating the transition from long-range order to al-gebraically decreasing correlation. This transition into the incommensurate solid should show up in a power-law peak profile. However, because of the low-peak intensities in our experiment a definite fit of the peak profiles was not possible.

In conclusion we found the commensurate-incommensurate transition of the fourfold degenerate $(2\sqrt{2}\times\sqrt{2})$ structure of CO/Pd(100) to be in the Pokrovsky-Talapov universality class where a commensurate solid turns into an incommensurate floating solid. The critical exponent for the incommensurability was determined to be 0.5 ± 0.05, and no indications of hysteresis have been detected. An exponent of 0.5 was also found for a CIT in another uniaxial adsorbate system, i.e., the $c(2\times2)$ phase of Xe/Cu(110).[13] But, in contrast to the CO/Pd(100) $(2\sqrt{2}\times\sqrt{2})$ phase the $c(2\times2)$ is only twofold degenerate, which should render the incommensurate floating phase unstable and the observed transition is rather a melting of the solid into the disordered phase than a CIT.[4] Our x-ray data further prove the domain-wall picture to be appropriate for the description of the incommensurate adlayer phase in CO/Pd(100).

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