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# X-Ray Scattering Study of the Commensurate-Incommensurate Transition of Monolayer Krypton on Graphite

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We describe an x-ray scattering study of the commensurate-incommensurate transition in monolayer Kr films physisorbed onto basal planes of *z-y-x* exfoliated graphite. At temperatures of 80.0 and 89.3 K there appears to be a single hexagonal-commensurate–to–hexagonal-incommensurate transition which is at least nearly second order with mean exponent $\beta = 0.30 \pm 0.06$. In the incommensurate phase we directly observe domain-wall superlattice effects.

The commensurate-incommensurate transition (CIT) of monolayers physisorbed onto simple surfaces is a topic of considerable current theoretical and experimental interest.[1-4] One of the more extensively studied examples of such a transition is Kr adsorbed onto the (0001) basal plane of graphite. At submonolayer densities, Kr forms a commensurate $(\sqrt{3}\times\sqrt{3})30°$ structure, with one atom per three graphite hexagons.[1,5] At higher surface density, but still in the first layer, the Kr lattice becomes incommensurate with respect to the graphite substrate. Low-energy–electron diffraction (LEED) measurements by Chinn and Fain[1] have shown that the phase change is apparently a second-order transition from a hexagonal commensurate (HC) structure to a hexagonal incommensurate (HI) structure. The LEED results were interpreted in terms of a one-dimensional dislocation theory[6]; however, more recent theories have emphasized that the two-dimensional nature of the adsorbate modulations is essential.[2] These theories predict either a single first-order transition or two successive transitions, one second order and the other first order. We shall discuss these theories in the context of our experimental results; at this point we need only emphasize that the above theoretical predictions are at variance with the apparently continuous single CIT observed with LEED. Recently, Horn *et al.* have shown that x-ray scattering may provide detailed information about surface phase transformations.[5] Specifically, x-ray diffraction techniques offer quantifiable intensities, negligible multiple scattering, and higher resolution than that available with LEED. Accordingly, we have undertaken a detailed x-ray study of the Kr monolayer CIT.

The experiments were performed on a two-axis x-ray spectrometer using the techniques and spectrometer configuration described in Ref. 5. The measurements were carried out in such a way that the vapor pressure, total amount of gas adsorbed, and the Kr(10) diffraction profile were determined simultaneously. We show in Fig. 1 a series of scans at four different coverages at 89.3 K. For all vapor pressures below 0.75 Torr, the peak has the sharp commensurate line shape shown in the upper panel. As the vapor pressure is increased beyond 0.75 Torr (second panel), the peak broadens. This increased linewidth near the CIT has also been observed in experiments on $H_2$ and $N_2$.[3] When the vapor pressure is further increased above 1.17 Torr, the peak position shifts from its commensurate value, $Q_{\text{comm}}$, to $Q_{\text{comm}}+\epsilon$, and a satellite peak appears at $Q_{\text{comm}}-\frac{1}{2}\epsilon$ (third panel). Finally, as shown in the lowest panel, the secondary peak disappears continuously with increasing incommensurability.

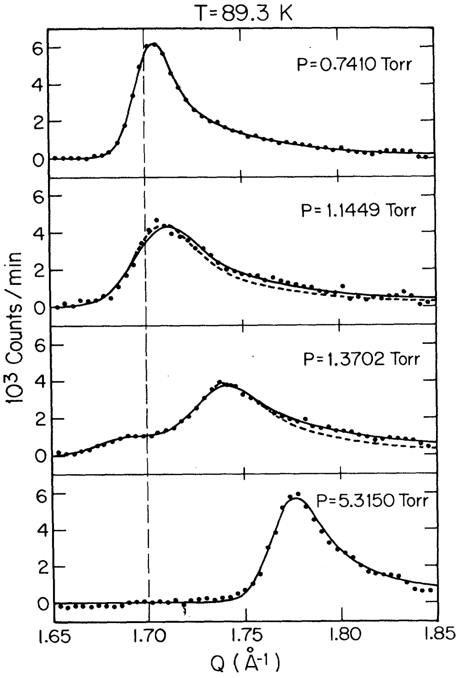

FIG. 1. X-ray scans of the Kr(10) line, less the graphite background. The solid lines are the results of the fits as described in the text, with all parameters varied. For the broken-line fits, the vertical mosaic was fixed at 14°. The vertical broken line is the position of the fitted commensurate peak.

It is evident from these scans that the CIT for Kr on graphite is rather more complicated than indicated by the LEED data. In order to discuss this quantitatively, it is necessary to carry out accurate fits to the measured x-ray profiles. The peaks were analyzed using the following model. An individual crystallite of linear dimension $L$ gives rise to Gaussian Bragg scattering with in-plane half width at half maximum (HWHM) $\pi/L$. This is then azimuthally powder averaged to account for the random orientation of the graphite (1000) and hence Kr(10) axes. This powder averaging represents the principal disadvantage of the x-ray experiments relative to LEED. Next, we include the mosaic distribution of the graphite (0001) planes. Because of the Bragg *rod* nature of the Kr scattering, a crystallite tipped out of the plane by an angle $\psi$ gives rise to an apparent in-plane wave vector increased by $1/\cos\psi$. This causes the peaks to be broadened to the high-$Q$ side. Finally, the theoretical line shape is convolved with the Gaussian longitudinal resolution function of HWHM 0.008 Å$^{-1}$. For the two-peak profiles (third panel), we first determined empirically that of the principal peak position was at $Q_{\text{comm}}+\epsilon$, the satellite peak was centered about $Q_{\text{comm}}-\frac{1}{2}\epsilon$. We then assumed that the satellite has an identical line shape to the primary peak. At the temperatures and coverages considered here, the density of atoms on the second layer is insignificant, at least insofar as line-shape phenomena are concerned.

The solid lines in Fig. 1 represent the results of the fits with all parameters allowed to vary freely. The results from these fits, together with the vapor-pressure isotherm, are shown in Fig. 2. It is evident that the data are consistent with a single, at least nearly second-order HC-to-HI phase transition at $\ln P=0.156$. We have obtained equivalent results in a separate set of experiments at $T=80.0$ K. Before beginning a detailed discussion of these results we draw attention to one apparent oddity. As shown in Fig. 2, the fitted graphite vertical mosaicity (there labeled "skewness") increases drastically from 14° to 21° near the transition. We show as dashed lines in the second and third panels of Fig. 1 the line shape with the vertical mosaicity parameter fixed at the value of 14°. This shows that the increase in the fitted vertical mosaicity near $\ln P_c = 0.156$ reflects an increase in the high-$Q$ scattering. We discuss this result below.

It is of interest to determine the extent to which the incommensurability $\epsilon$ exhibits a simple power-law dependence on the chemical-potential difference $\mu - \mu_c \propto \ln(P/P_c)$. We show in Fig. 3 the results of least-squares fits of a single power law $\epsilon = \epsilon_0 \ln^{\beta}(P/P_c)$ to the data at 89.3 and at 80.0 K. For both temperatures, one finds a good fit for $0.002\ \text{Å}^{-1} \leq \epsilon \leq 0.06\ \text{Å}^{-1}$ with exponents $\beta = 0.32 \pm 0.02$ and $0.26 \pm 0.06$ at 89.3 and 80.0 K, respectively. For $\epsilon \leq 0.002\ \text{Å}^{-1}$ the transition appears to be rounded, presumably due to finite-size effects.[5]

We now discuss the interpretation of these results. To our knowledge, no theoretical treatment of CIT's has taken the chemical potential of the adsorbate as the independent variable. However, several authors have made the approximation that the unstrained bond length is simply related to chemical potential, and solved the related problem of an overlayer with a given natural spacing. In a classic set of papers,[6] Frank and van der Merwe (FvdM) considered the phase transition behavior of an overlayer with unstrained spacing $b$, on a substrate consisting of a sinusoidal potential with period $a$. They solved this problem in the mean-field approximation at $T = 0$, assuming a one-dimensionally modulated incommensurate state. As $b$ decreases below $a$, FvdM found that the system will retain the periodicity $a$ down to a critical value $b^*$ of the unstrained adsorbate spacing. For $b < b^*$, the adsorbate breaks up into locally commensurate regions, separated by a lattace of domain walls. With decreasing $b$, the domain walls merge, approaching a uniform phase with lattice constant $b$. FvdM predicted that the resulting lattice misfit will vary logarithmically with $b^* - b$ near the critical value. This corresponds to a second-order phase transition with exponent $\beta = 0$. The FvdM theory considers only one-dimensional modulations. However, Bak *et al.*[2] have emphasized that for overlayers on graphite, the modulations are two dimensional; one must consider the energetics of domain-wall crossings. At $T = 0$, they predict either a single HC-to-HI *first-order* phase transition or a second-order transition from the HC phase to a one-dimensionally modulated (and therefore nonhexagon) phase, followed by a first-order transition into the HI phase.

Our results for Kr on graphite confirm the dislocation descriptions of the incommensurate

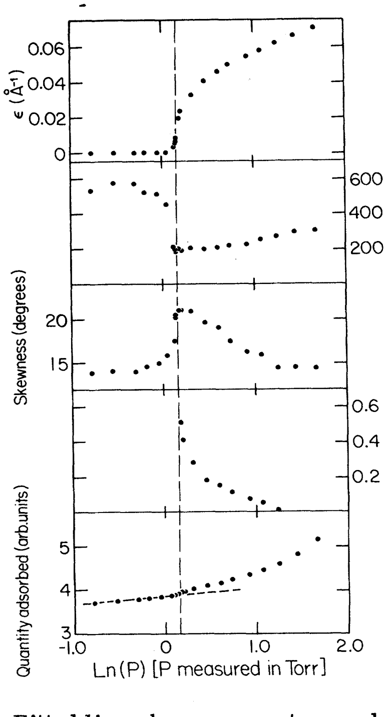

FIG. 2. Fitted line-shape parameters and quantity of adsorbed Kr, as functions of $\ln P$ for $T = 89.3$ K.

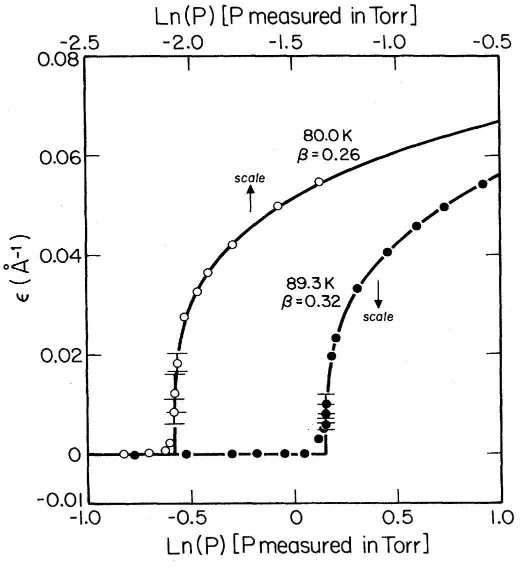

FIG. 3. Fitted peak position vs $\ln P$ for $T = 80.0$ and 89.3 K. Note the different pressure scales. Curves are the results of power-law fits described in the text.

phase. The two-peak structure observed in the HI phase near the transition almost certainly comes from an array of domain walls. In calculations of the diffraction pattern from hexagonal superlattices of atoms, we obtain principal peaks at $|Q| = Q_{\rm comm} + \epsilon$ and $|Q| = Q_{\rm comm} - \frac{1}{2}\epsilon$.[7] At larger incommensurability, the $Q_{\rm comm} - \frac{1}{2}\epsilon$ satellite peak decreases in magnitude, indicating that one is approaching a uniform incommensurate phase. Indeed, as suggested by Hastings and Moncton, the satellite peak can be thought of as reflecting a strain modulation of the incommensurate Kr lattice due to the substrate.[4] To lowest order, this strain will generate satellite peaks at $\vec{Q}_{\rm graphite} + \vec{Q}_{\rm Kr}$ which, in a powder pattern, appear as a single peak at $Q_{\rm comm} - \frac{1}{2}\epsilon$. We emphasize, however, that given the strength of the satellite peak near the CIT, the scattering in this region is best thought of in terms of misfit dislocations rather than a weak perturbation on the incommensurate Kr lattice.

As we noted previously, there is considerable extra scattering on the high-$Q$ side of the diffraction peak near $P_c$. While this may arise partially from unresolved higher-order satellites, we believe that it is primarily due to regions around interstitials where the atoms have density higher than that given by the lattice constant. In that case, the increase of the fitted vertical mosaic just below $P_c$ may represent entry into an overcompressed regime ($b^* < b < a$). FdvM predict that with increasing misfit, the structure gradually approaches a uniform state; indeed we find that the extra high-$Q$ scattering disappears with increasing coverage. Notably, the vanishing of this high-$Q$ scattering coincides approximately with the disappearance of the satellite peak. As mentioned above, current theories suffer from the shortcoming that they neglect the energy and entropy of interstitial atoms in the nominally commensurate phase; hence they cannot describe such line-shape phenomena. More detailed models are needed before we can definitely assign the increase in skewness to interstitials.

We also observe dramatic variations in the Kr-crystallite coherence distance $L$. In the HI phase far from $P_c$ we have $L \simeq 300$ Å, compared with $L \simeq 600$ Å in the HC. Assumedly this reflects an enhanced sensitivity of the incommensurate Kr overlayer to surface pinning effects, etc. $L$ is a minimum at $P_c$, perhaps indicating maximum susceptibility at that point.

Finally, we consider the critical behavior. As illustrated in Fig. 3 the experiments are consistent with a single HC-to-HI transition with critical exponent $\beta = 0.32 \pm 0.02$ at 89.3 K and $\beta = 0.26 \pm 0.06$ at 80.0 K. The LEED experiments which were carried out at $T = 54-59$ K also indicate a second-order CIT albeit with rather less certainty. The LEED measurements were interpreted in terms of the FdvM theory, which would imply $\beta = 0$. This apparent difference in exponents probably simply reflects the improved accuracy of our x-ray measurements, although the effective value of $\beta$ could be temperature dependent. This might arise either from the existence of a marginal variable, or from crossover between the $T = 0$ and finite-$T$ exponents. We find no direct evidence for the stripe-domain phase predicted by Bak *et al.*, nor for any first-order transition between the HC and HI phases.

In short, there is no current theory that correctly describes the observed CIT for Kr on graphite, although certain of the qualitative features are correctly predicted by FdvM. We hope, in particular, that our experiments will stimulate discussion of models which use chemical potential rather than bond length as the independent variable and transcend the continuum elastic description of the adsorbate.

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[7] A configuration in which hexagonal domains are oriented parallel to the graphite hexagons, with a phase shift of two sites across a wall, gives peaks at $Q_{\mathrm{comm}}+\epsilon$ and $Q_{\mathrm{comm}}-\frac{1}{2}\epsilon$. These occur at the same places in reciprocal space as the spots observed by LEED (Ref. 1).

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# Wall-Induced Pretransitional Birefringence: A New Tool to Study Boundary Aligning Forces in Liquid Crystals

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A wall-induced birefringence in a nematic liquid crystal above the nematic-isotropic phase transition point has been observed for the first time. It is expected that this phenomenon will provide a useful tool to study the nature of aligning forces at liquid-crystal–solid interfaces.

It is well known[1] that by a suitable treatment of a substrate surface, one can impose a specific director orientation in a liquid crystal (LC) film. It is supposed that the wall aligns the adjacent LC molecules by exerting anisotropic forces of some physicochemical nature; the bulk of the film is then aligned as a result of the director elasticity.[2] The wall, thus, acts as an external field and therefore will induce birefringence above the nematic-isotropic phase transition temperature ($T_c$) just as a magnetic, electric, or shear-flow field does. In this Letter, the first observation of the wall-induced birefringence is reported. The effect is naturally very sensitive to differences in orienting force and is expected to be a useful tool to study the microscopic origin of the aligning forces at LC-solid interfaces.

A wall-induced alignment in the isotropic phase of nematics has been previously analyzed theoretically.[3] A simple sketch of the treatment using the Landau–de Gennes theory is appropriate here. The Landau–de Gennes free energy density is given by[4]

$$F=F_0+F_1(Q)+\tfrac{1}{2}L\,|\nabla Q|^2, \tag{1}$$

where

$$F_1(Q)=\tfrac{1}{2}AQ^2-\tfrac{1}{3}BQ^3+\tfrac{1}{4}CQ^4, \tag{2}$$

where $F_0$ is that part which does not depend on the order parameter, $Q$. It is usually assumed[4] that $A=a(T-T^*)$ and $a$ together with $B$, $C$, $L$, and $T^*$ are material constants. When the wall imposes some orientation on the LC molecules, the order parameter at the wall, $Q_b$, is not zero even above $T_c$. Let us take a Cartesian coordinate system where $z=0$ defines the wall and the $z$ axis points into the LC. With the assumption that $Q$ depends only on $z$, the minimization of the volume integral of Eq. (1) yields

$$\xi_0^2(dQ/dz)^2=f(Q), \tag{3}$$

with $Q(z=0)=Q_b$ and $Q(z=\infty)=0$; here $\xi_0^2=L/aT^*$ and $f(Q)=F_1(Q)/aT^*$. In Eq. (3) it is assumed that the sample is thick enough so that the effect of the other side of the film is negligible.[5] In the first approximation, the phase difference, $\Delta\varphi$, of the ordinary and extraordinary rays due to the birefringence of the film is proportional to

$$\Delta\varphi\sim\int_0^\infty Q(z)dz\,. \tag{4}$$

Equation (4) was calculated numerically using a set of parameters pertinent to pentyl-cyanobiphenyl (5CB) from Coles[6] and assuming $\xi_0=6$ Å.[7] The result is shown in Fig. 1 for different values of $Q_b$ as a function of temperature. The sudden increase of the pretransitional divergence for $Q_b$

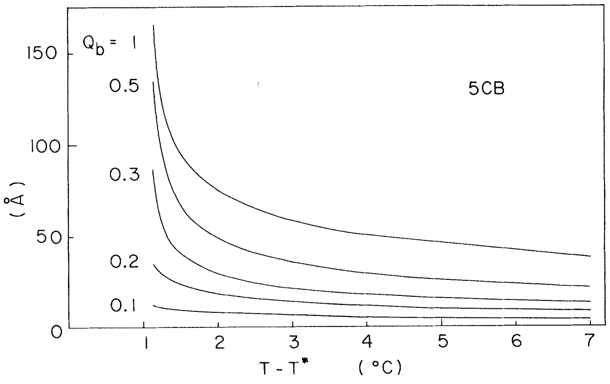

FIG. 1. Numerical calculations of $\int_0^\infty Q(z)dz$ for several boundary values, $Q_b$, as a function of temperature.