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Pressure-Driven Commensurate-Incommensurate Transition in Low-Temperature Submonolayer Krypton on Graphite

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By using D_2 gas as a source of two-dimensional spreading pressure, we have studied the commensurate-incommensurate (C-I) transition in submonolayer Kr on ZYX graphite at temperatures near 40 K. High-resolution synchrotron x-ray diffraction results show both hysteresis and C-I phase coexistence, clear signatures of a first-order transition. This agrees with theoretical predictions, but apparently gives different behavior from earlier studies at higher temperatures and coverages.

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When a thin film is deposited on a crystalline substrate, the competition between adsorbate-adsorbate interactions and the adsorbate-substrate lateral periodic potential can produce a structure which is either commensurate with the substrate or incommensurate, depending on the misfit between the substrate and the natural adsorbate lattice spacings. The resultant misfit depends on the temperature and the two-dimensional (spreading) pressure. Although there have been detailed structural studies¹⁻⁴ of near monolayer films at elevated temperatures, as well as extensive theoretical work on the nature of the commensurate-incommensurate (C-I) transition, the overall situation is far from being understood. To quote Villain⁵: "Conclusion: either the C-I transition is first order or the hexagonal symmetry is destroyed near the transition. There is no well established confirmation of this theoretical prediction. Krypton monolayers on graphite. . . seem to provide a counterexample. . . it would be interesting to have data at low tempera-

tures which are more accessible to theory." We report such a high-resolution study here.

Two experimental ingredients have been crucial in making this possible. The first is a means of continuously adjusting the surface pressure at submonolayer coverages and at temperatures well below the melting point of the Kr film. This has been done by adding D_2 gas, which is insoluble in the Kr film, and whose spreading pressure can be controlled even at constant temperature by adjusting its bulk vapor pressure. It thus acts as a two-dimensional piston pushing on the Kr film. The second ingredient is the use of the synchrotron source at Hasylab, Hamburg, to provide the intense collimated x-ray beam required for very-high-resolution line-shape studies in the transition region.

Three independent tests on an 0.6-monolayer Kr sample at temperatures near 40 K all point to a first-order C-I transition. These are line-shape studies in the C-I coexistence region and hysteresis loops both as a function of surface

spreading pressure at constant temperature and as a function of temperature at constant D_2 filling. This first-order behavior is in agreement with low-temperature theoretical predictions,⁵⁻⁸ but is apparently different from that previously observed^{3,4} at higher temperatures, and coverages, where the driving force is the spreading pressure of Kr itself.

The x-ray diffraction was carried out with use of a triple-axis spectrometer. The center part (0.2 mrad) of the 1-mrad white beam (D4) of the storage ring DORIS ($E = 3.285$ GeV, 50 mA) hits a perfect Ge crystal monochromator in the (1,1,1) horizontal reflection orientation and produces a highly collimated monochromatic beam at $\lambda = 1.4809$ Å. The direction of the scattered beam is determined by a similar Bragg reflection from a Ge analyzer crystal utilizing the fact that the scattering is elastic. The resulting wave-vector resolution around the (1,0) Kr peak is 0.00045 Å⁻¹ half width at half maximum (HWHM), and so correlation ranges up to several thousands of angstroms are measurable.

The graphite substrate is Union Carbide ZYX in transmission with a vertical common c axis. After bakeout at 800 °C the substrate was transferred in a glove box to a sealed cell with Be windows. The cell is connected via a capillary to a standard filling volume outside the Displex cryostat. The pressure is determined by a Baratron pressure gauge to an accuracy of 0.1% and the temperature is held constant to within 10 mK.

We have previously found that the C-I transition in pure Kr around 40 K is of first order,⁹ based on x-ray spectra showing coexistence much like those to be described below. We use this to establish the scale of registered coverage by asserting $\rho = 1$ just when signs of the coexisting incommensurate phase become visible in pure Kr film samples. The scale of coverage was determined before and after the measurements of the D_2 -induced C-I transition.

Figure 1 shows two scans taken at $T = 39.44$ K on a sample having a Kr coverage of 0.6 registered monolayer. Below a D_2 vapor pressure of 4.5 Torr only a commensurate (1,0) Kr peak is observed, centered at $Q_0 = 1.703$ Å⁻¹. The HWHM of the leading edge is 0.003 Å⁻¹, corresponding to a coherence length $L \approx 1200$ Å. It should be noted that the (1,0) peak of a pure Kr film at the same coverage and temperature is somewhat sharper ($L = 1600$ Å). This agrees with the previous synchrotron results of Birgeneau *et al.*¹⁰ for registered Kr on ZYX graphite. Note that the leading

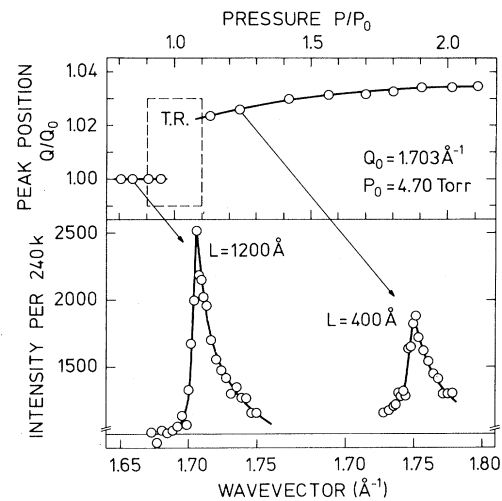


FIG. 1. Data at $T = 39.44$ K and a Kr coverage of 0.6 monolayer. Top part: Lattice compression relative to the registered lattice by an applied two-dimensional pressure of a fluid D_2 film. The pressure P is the vapor pressure of D_2 . "T.R." denotes transition region. Bottom part: Commensurate (left) and incommensurate (right) line profiles of the (1,0) Bragg reflection. The sharpness of the leading edge determines the coherence length L .

edge reaches the background level abruptly; there is no "wing."

Above $P_{D_2} = 5$ Torr only a well-developed incommensurate peak is observed, whose position shifts with applied D_2 pressure. A typical example, taken at $P_{D_2} = 5.3$ Torr is shown at the right-hand side of Fig. 1. The HWHM is 0.006 Å⁻¹, twice the value in the commensurate phase. Note the wing on the leading edge, a characteristic signature of the quasi-long-range order of a floating two-dimensional solid. The small degradation of L in going from a pure Kr film to a registered phase with a D_2 vapor pressure 10% below the transition pressure and the larger change in L in going all the way to the incommensurate phase may be understood qualitatively by the presumably much larger susceptibility to defect strain of the incommensurate phase.

Changes of the spreading pressure $\Delta\phi_1$ on the Kr monolayer can be estimated in two ways. It is related to the compressibility K by $\Delta\phi_1 = K^{-1}(\Delta Q/Q_0)^2$. Calculation of K is trivial in the fully developed incommensurate phase since lateral substrate forces may be neglected, but this simplification is not valid near the transition region where the domain structure is the prominent feature. Another estimate is to equate $\Delta\phi_1$ with $\Delta\phi$, the

change of the overall Gibbs pressure, thereby neglecting the fact that not all D_2 molecules are in the first layer. This approximation is probably fairly accurate and yields $\Delta\varphi_1 \approx (kT/a)\Delta P/P$, where a is the area of a D_2 molecule and P the vapor pressure of D_2 . In the pressure range labeled T.R. (transition region) the form of the scattered intensity $S(Q)$ is complex. Figure 2 shows three scans taken at constant D_2 filling ($\rho_{D_2}=0.49$, $\rho_{Kr}=0.60$) as a function of temperature, which affects φ_1 by changing the fraction of D_2 molecules adsorbed. Here two features are clearly seen. Above the highest temperature shown only a single peak similar to that shown in Fig. 1 is observed at the registered position Q_0 . With decreasing temperature (increasing φ_1) intensity is progressively shifted from the Q_0 peak to one centered at $Q=1.733 \text{ \AA}^{-1}$. At $T=33.24 \text{ K}$ the low- Q group has shifted to *below* the registered position, and is centered at $Q=1.69 \text{ \AA}^{-1}$. This set and similar isothermal pressure scans indicate that there is a phase coexistence between a commensurate structure ($Q_0=1.703 \text{ \AA}^{-1}$) and an

incommensurate lattice containing hexagonal domain-wall superstructure modulation. Such a structure would have its main peaks at $Q_0 + \epsilon$ and $Q_0 - \epsilon/2$.^{3,6} The value of ϵ depends on the degree of compression, and our data in the transition region ($T \approx 40 \text{ K}$) indicate an $\epsilon = 0.03 \text{ \AA}^{-1}$. The weak $-\epsilon/2$ peak is buried in the Q_0 one until almost all the registered phase has gone. The ratio of 7:2 of the $+\epsilon$ and $-\epsilon/2$ peaks indicates that a significant fraction of the Kr atoms are in the domain walls. Further decrease in temperature or increase in pressure causes ϵ to increase and the peak at $-\epsilon/2$ to rapidly lose intensity, thus developing the typical completely incommensurate pattern shown on the right-hand side of Fig. 1. Calculated curves compatible with these results are shown on the right-hand side of Fig. 2, including the intensity decompositions. The leading edges of the three components are twice as broad (0.012 \AA^{-1} HWHM) as that of the purely incommensurate phase. This may be due to a "melted" domain structure (Villain⁵ and Coppersmith *et al.*¹¹) where the sizes of the hexagonal domains fluctuate.

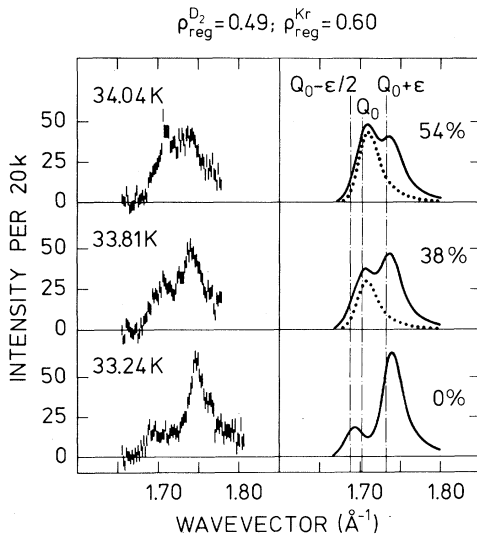


FIG. 2. Line profiles in the transition region at constant D_2 filling. With increasing temperature D_2 is evaporated from the film and the two-dimensional pressure decreases. The line profiles at the right are calculated by using fixed values of the ratio between the intensities of the $+\epsilon$ and $-\epsilon/2$ peaks (7:2), the coherence length $L=250 \text{ \AA}$, and $\epsilon=0.03$. The only varying parameter is the relative intensity of the commensurate phase, given in percent in the figure and with a line profile as shown by the dotted line. At 34.04 K the commensurate and the incommensurate phases thus coexist in approximately even proportions.

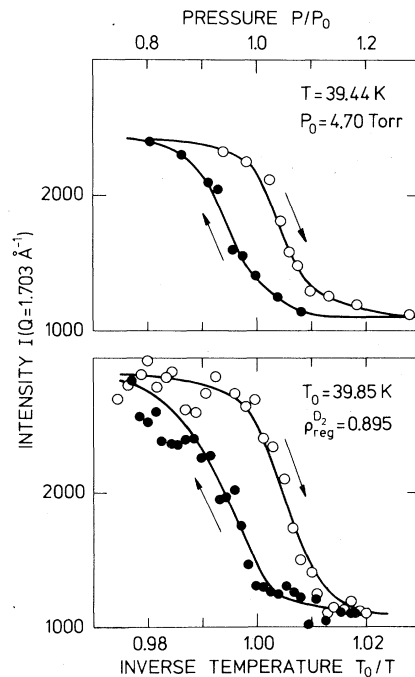


FIG. 3. Hysteresis loops of the C-I transition. In the top part the vapor pressure of D_2 is varied at constant temperature; in the bottom part the temperature is varied at constant filling. The full lines are guides to the eye. The ratio of the widths of the two hysteresis loops agree with a simple thermodynamic argument given in the text.

In addition to phase coexistence, hysteresis caused by a nucleation barrier is a common signature of a first-order phase transition. Such loops of the intensity at $Q_0 = 1.703 \text{ \AA}^{-1}$ are shown in Fig. 3, both as a function of temperature at constant Kr coverage and D_2 filling, and as a function of D_2 pressure at constant temperature and Kr coverage. Because of the presence of the D_2 vapor, thermal equilibrium is rapidly reached in the Kr films, unlike the case for low-temperature pure Kr. We find that the observed spectra reach a constant shape within a few minutes after a small temperature change and maintain that for at least 10 h.

While the temperature hysteresis loop is sharp ($\Delta T/T_0 \approx 2\%$), that in pressure is an order of magnitude broader ($\Delta P/P_0 \approx 20\%$). Such behavior is expected from thermodynamic considerations. We assume that for small changes $\Delta\phi_1$ is proportional to $\Delta\phi$. The controlling factor for the width of the hysteresis loops should be the difference in chemical potentials, or spreading pressures, across the loops. The relative widths are then given by $(\partial\phi/\partial\ln P)_T$ and $(\partial\phi/\partial\ln T)$ at constant D_2 filling. The Clausius-Clapeyron relation gives for D_2 ⁷

$$\left(\frac{\partial\phi}{\partial T}\right) = \frac{s_{\text{film}} - s_{\text{gas}}}{a_{\text{film}}} = \frac{q_{\text{eq}}}{a_{\text{film}}T},$$

where q_{eq} is the equilibrium heat of adsorption, $q_{\text{eq}} = q_{\text{st}} - \phi a_{\text{film}}$. Here q_{st} is the isosteric heat of adsorption, given by $(\partial\ln P/\partial T) = q_{\text{st}}/k_B T^2$. The Gibbs isotherm gives $(\partial\phi/\partial P)_T = k_B T/aP$. Our measured value for q_{st} is $-390 k_B \cdot K$, giving $q_{\text{eq}} \approx -300$ to $-350 k_B \cdot K$. Thus at $T = 40 \text{ K}$ we find $(\partial\phi/\partial\ln P) : (\partial\phi/\partial\ln T) \approx -1:8$. Although this can explain the relative widths of the two hysteresis loops, the finite slopes in the pressure plot require some heterogeneity.

Previous low-energy electron-diffraction^{1,2} and x-ray^{3,4} work as well as a recent synchrotron x-ray study¹² of the C-I transition in Kr films have used the Kr vapor pressure as the driving force. Thus, these experiments always involve a complete monolayer and relatively high temperatures. These experiments were all interpreted as the transition being of second order. Our results show unambiguously that the transi-

tion at submonolayer coverage and relatively low temperatures is of first order. It would be of interest to extend the present studies to higher temperatures and coverages and observe the gradual changes (if any) of the C-I transition with ρ and T , including the possibility of a C-I critical point. We plan to do so in the near future.

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