

## 9.0 X-Ray Diffuse Scattering

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In this research program, modern x-ray scattering techniques are used to study structures and phase transitions in thin films and on surfaces. We have two principal experimental facilities. At MIT we have four high-resolution computer-controlled x-ray spectrometers using high intensity rotating anode x-ray generators. The angular resolution can be made as fine as 1.8 seconds of arc; this enables one to probe the development of order from distances of the order of the x-ray wavelength,  $\sim 1\text{\AA}$ , up to  $30,000\text{\AA}$ . The sample temperature may be varied between 2K and 500K with a relative accuracy of  $2 \times 10^{-3}\text{K}$ . We also have, in collaboration with IBM, a two spectrometer system at the National Synchrotron Light Source at Brookhaven National Laboratory. A third beam line designed to operate at short wave lengths is currently being implemented. These make possible high resolution scattering experiments with a flux more than three orders of magnitude larger than that from a rotating anode x-ray generator; this, in turn, has opened up a new generation of experiments.

As part of this JSEP program we have built an x-ray compatible high vacuum single crystal apparatus. This enables us to use synchrotron radiation to study the structure and transitions occurring at a single surface; the first generation of such experiments has now been performed. Our current experiments in this program are concentrated in two areas: 1) the phases and phase transitions of metal and semiconductor surfaces and surface overlayers; and 2) the structure and phase transitions of rare gas multilayers on simple substrates.

### 9.1 Metal Surface Studies

For our first detailed studies of metal surface reconstruction we have chosen tungsten, both pure and coated with hydrogen or oxygen. The tungsten system has been exhaustively studied with all of the standard surface techniques including LEED, STM, atom beam scattering, and Rutherford back scattering. In spite of this effort, there are still major controversies concerning the nature of the structures and surface transitions. Our most successful experiments were for W (100) with sub-monolayer coverages of H.

The system of atomic hydrogen chemisorbed onto the surface of tungsten has long been considered a model system for the study of chemisorption. Extensive experimental

studies have shown that the W(100) surface goes through an elaborate sequence of phases and phase transitions as a function of increasing hydrogen coverage; however, the microscopic nature of these successive states remains problematic. We carried out a synchrotron x-ray glancing-angle diffraction study of W(100) at room temperature for a range of hydrogen coverages. The experiments illustrate clearly the utility of x-rays in obtaining quantitative information about the structures and the nature of the disorder in such chemisorbed surface systems.

Our data suggest a simple picture in which at very low coverages there is a tradeoff with increasing coverage, analogous to that in a two-phase coexistence region, between hydrogen-poor and hydrogen-rich regions until a uniform but still disordered  $(\sqrt{2} \times \sqrt{2})R45^\circ$  -H phase is attained. This disagrees with the currently accepted model which assumes that the hydrogen atoms are always uniformly distributed on the tungsten surface. With further increase in coverage the surface layer exhibits a commensurate-incommensurate transition (CIT) which, rather than being a solid-solid transition as previously assumed, is actually a lattice-gas melting transition into a domain-wall fluid phase. Such surface domain-wall fluid phases should occur commonly in chemisorbed systems.

We find that the line-shape in the  $(\sqrt{2} \times \sqrt{2})R45^\circ$  -H phase is well-described as a Lorentzian raised to the 3/2 power. This line-shape is indicative of random field effects in two dimensions. Specifically, in surface lattice-gas systems, impurities and defects which fix the sublattice locally act as random fields which round the freezing transition and prevent the achievement of true long range order. Such random field effects have not been seen in previous surface diffraction experiments; only x-rays provide the resolution and simple kinematical interaction to allow such quantitative line-shape analysis.

## 9.2 Rare Gases on Graphite

In the last year, we completed two major experiments on monolayer rare gas films. First we carried out an encyclopaedic high resolution x-ray diffraction study of the structures and phase transitions of monolayer krypton, adsorbed on both powder and single crystal graphite substrates. A comprehensive series of powder diffraction profiles was used to construct the two-dimensional phase diagram. The melting of the commensurate solid was shown to be strongly first order throughout the region where tricritical behavior was previously thought to occur; fluid-solid coexistence extends up to the termination of the commensurate phase at 130 K. A disordered, weakly incommensurate phase with lattice constant smaller than that of the  $\sqrt{3} \times \sqrt{3}$  phase was shown to be reentrant fluid, a system which may be described as a disordered network of domain walls and which evolves continuously into a more conventional 2D fluid. This evolution is marked by the disappearance of satellite peaks which are caused by the modulation of the overlayer by the substrate. The freezing of the reentrant fluid into the commensurate phase was shown to be consistent with a chiral Potts transition, its freezing into the incommensurate solid consistent with a dislocation binding transition. Single crystal experiments revealed the orientation of the weakly incommensurate phase. The reentrant fluid was found to have no visible orientational fluctuations, manifesting isotropic diffraction peaks. This is attributed to the strong epitaxy of domain walls. The incommensurate solid was shown to undergo an aligned-rotated transition which is well described by zero-temperature calculations.

Second, we carried out an extensive synchrotron x-ray study of monolayer xenon on single crystal graphite. A monolayer of xenon freezes at  $\sim 135\text{K}$  into an incommensurate solid. The incommensurate solid undergoes the sequence of phases with decreasing temperatures aligned  $\rightarrow$  rotated  $\rightarrow$  reentrant aligned, before transforming at  $\sim 70\text{K}$  into a commensurate  $\sqrt{3} \times \sqrt{3} R45^\circ$  solid. The current theory of orientational epitaxy correctly predicts only the point at which the rotated  $\rightarrow$  reentrant aligned transition occurs. None of the current theories can explain the entire sequence. The reentrant aligned phase at intermediate temperatures is an incommensurate solid with a network of superlight domain walls. The observed phase transition into the commensurate phase is first order consistent with domain wall theories. The incommensurability decreases as

$$\left[ \frac{T - T_0}{T_0} \right]^{1/3}$$

until the first order C-IC transition point is encountered. This  $1/3$  power law is apparently a universal behavior shared with Kr on graphite.

We have estimated the potential corrugation of the surface adsorption from the intensity ratios between the main and satellite peaks in the domain wall incommensurate phase. The corrugation of the potential estimated is close to that predicted by Steele. Along with this estimation from the onset of the rotated phase, we are able to set the limits for the dimensionless wall width,  $36 < \ell_0 < 42$ . Also we estimated the wall crossing energy which turned out to be  $+60\text{K}$ . However, the striped phase, predicted by Halpin-Healy using a similar value was not observed.

### 9.3 Surface Roughening of Ag

Direct evidence of the thermal roughening of Ag (110) surface has been observed in a high resolution x-ray scattering experiment at the National Synchrotron Light Source of the Brookhaven National Laboratory. Information about the surface roughness, as manifested in the height-height correlation function, is obtained from the scattering intensity profile of the bulk forbidden  $(\bar{1}\bar{1}0)$  surface peak. The results indicate that surface roughening occurs at  $T_r = 450 \pm 25^\circ\text{C}$ . Below  $T_r$ , the Ag (110) surface is smooth, as characterized by delta function Bragg scattering, whereas above  $T_r$ , the scattering intensity obeys a power law lineshape, indicating a rough surface with logarithmically divergent height fluctuations. Since the transition is reversible with temperature, it is indeed an equilibrium phase transition. Furthermore, the fact that the integrated intensity of the bulk Ag (111) peak undergoes little change during the transition, apart from the Debye-Waller factor, demonstrates that the observed changes in bulk forbidden  $(\bar{1}\bar{1}0)$  peak are due exclusively to changes in the surface morphology. In contrast to atom scattering and LEED experiments which have significant multiple scattering and inelastic scattering, x-ray experiments allow relatively simple data analysis. Coupled with the high resolution of our experiment, we have demonstrated a very powerful technique for studying surface roughening.

## Publications

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