

## VII. X-RAY DIFFUSE SCATTERING

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This research program centers around a two-spectrometer x-ray diffuse-scattering system based on a Rigaku 12-kW rotating-anode x-ray generator. The apparatus is designed in such a way that one may easily tailor the instrumental resolution function to optimize studies of structure and fluctuations in a vast range of physical systems. Angular resolution of 1.8 seconds of arc and sample temperature control of 2 mK between 10 K and 500 K are available. We have implemented a position-sensitive detection system to allow rapid scans over a wide range of scattering angles, again with continuously variable resolution. Our current research program emphasizes structure and melting transitions both for monolayer physisorbed films on graphite and for layered liquid crystals. The surface experiments involve in situ high-precision vapor-pressure and surface-coverage measurements. Experiments are also performed using the x-ray synchrotron facilities at D.E.S.Y. (Hamburg, Germany) and S.L.A.C. (Stanford). We are currently designing a two-spectrometer high-resolution x-ray system to be permanently located at the National Synchrotron Light Source under construction at Brookhaven National Laboratory.

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### 1. MELTING AND THE COMMENSURATE-INCOMMENSURATE TRANSITION OF MONOLAYER KRYPTON ON GRAPHITE

We have effected an improvement by more than an order of magnitude of our studies of the structure and transitions of monolayer krypton on graphite by the use of x-ray synchrotron radiation techniques. The intensity and geometry of the synchrotron beam allows a resolution of  $3.5 \times 10^{-4} \text{ \AA}^{-1}$ , corresponding to a particle size of about 1 micron, with reasonable diffraction signals from one monolayer. We show that for ZYX graphite as a substrate the intrinsic krypton overlayer particle size is  $2300 \text{ \AA}$ . We find that, at one monolayer covering, the melting transition appears to be second order at  $112.9 \text{ K}$  with an order parameter exponent  $\beta = 0.065 \pm 0.015$  and a broadening of  $T_c$ ,  $\sigma/\langle T_c \rangle \sim 0.0006$  which we attribute to finite size. Although the broadening is much less than that obtained in coarser resolution experiments, the exponent  $\beta$  agrees with those previous results. Our most dramatic results are for the commensurate-incommensurate transition. We find that in the weakly incommensurate phase, the structure factor is that of a well-correlated liquid. This obtains for temperatures far below the expected melting temperature. We speculate that this is due to a melting of the domain-wall lattice. Recent theories, stimulated by this research, support this view. This work appears in several publications.<sup>1-3</sup>

### 2. MELTING OF 1.2 MONOLAYER XENON ON GRAPHITE

Xenon on graphite appears to provide a model example of continuous symmetry melting in two dimensions, albeit with a directional-ordering field from the substrate. Our previous work has shown that the melting transition is first order in the submonolayer region.<sup>3</sup> We have carried out an exhaustive study using x-ray diffraction techniques of the melting transition in the 1 to 1.5 monolayer region. We find that the solid phase is well described by a sharp Lorentzian line shape indicative of a  $1/q^2$  Landau-Peierls diffraction peak.<sup>3</sup> In the liquid phase we again obtain a Lorentzian profile, albeit with a measurable width. The evolution between these two profiles is continuous, as would be expected for a second-order transition. However, because of uniqueness problems, we can only

assert that the melting transition is nearly second order with a minimum liquid correlation length at melting of 50 Å. Much higher resolution measurements using synchrotron radiation techniques will be required to make a stronger statement. Such experiments are now scheduled at S.S.R.L.

### 3. STRUCTURE, PHASE DIAGRAM AND TRANSITIONS OF MONOLAYER AND BILAYER MOLECULAR OXYGEN ON GRAPHITE

Oxygen adsorbs onto graphite in the molecular state; the oxygen molecule is unique among homonuclear diatomic species in that it is paramagnetic with spin  $S = 1$ . The interplay between the magnetic, orientational, and structural degrees of freedom make both 3d and 2d oxygen rich and quite subtle. Previously, susceptibility and neutron-scattering studies of monolayer and bilayer oxygen on graphite have been performed. Both experiments suggest that oxygen solidifies at about 30 K for a monolayer and 40 K for a bilayer. The neutron studies suggest that the structure is triangular with a nearest-neighbor intermolecular spacing close to that in the bulk, and concomitantly, incommensurate with the graphite. The neutron studies also suggest that bilayer oxygen undergoes an antiferromagnetic transition at 11.9 K. We have carried out a detailed x-ray study of the structure of monolayer and bilayer oxygen as a function of coverage from 0.5 to 2.5 monolayers and of temperature from 12 K to 50 K. We find evidence for at least four distinct phases, only one of which is triangular. In particular, the bilayer phase is only triangular within 2 K of melting, in explicit contradiction with the neutron results. We have not yet managed to produce an unambiguous model for the bilayer structure, although the data are consistent with incommensurate successive layers. We find convincing evidence that at monolayer coverage the oxygen molecules lie flat on the graphite surface with a simple centered rectangular unit cell. Work on this system is continuing. Our first set of results has been published.<sup>4</sup>

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### 4. NEMATIC, SMECTIC A AND SMECTIC C PHASE TRANSITIONS AND CRITICAL BEHAVIOR IN $\overline{8S5}$ - $\overline{7S5}$ MIXTURES

We have carried out a series of high-precision measurements of the nematic-smectic A, smectic A-smectic C, and nematic-smectic A-smectic C triple-point critical behavior in a mixture of  $\overline{8S5}$  and  $\overline{7S5}$ . The triple point occurs at a concentration of  $\sim 42$  mole %  $\overline{7S5}$ . The SmA-SmC transition is mean-fieldlike in pure  $\overline{8S5}$ . However, near the N-A-C triple point there is a dramatic crossover from a tilt-order parameter exponent of  $1/2$  to  $1/3$  indicating true critical behavior. This crossover is undoubtedly driven by the simultaneous loss of the mass-density ordering. We find that critical fluctuations in the nematic phase are well described by a single Lorentzian for  $c \leq 0.42$  so that no unusual line-shape effects occur near the N-A-C point; this explicitly contradicts our own expectations and current theories. Away from the triple point we find single power-law behavior for the N-SmA transitions, albeit with exponents somewhat larger than those predicted by the superconducting analog model. However, in the vicinity of  $c = 0.42$ , we find continuously evolving exponents as one approaches  $T_c(N-SmA)$  with asymptotic exponents close to those of the 3d xy model. We do not fully understand these results. A letter and a full manuscript on this work are in preparation.

### 5. STRUCTURE OF WELL-ORDERED SMECTIC PHASES

We have carried out a number of diffuse x-ray scattering studies of the well-ordered smectic phases in the liquid-crystalline materials, 40.8, 40.7, and 6.05. We find in each case that the so-called smectic B phases are, in fact, extremely soft solids with three-dimensional positional long-range order. In 40.7 and 6.05 there are restacking transitions within the well-ordered phases in which one goes from an ABAB--- to an ABCABC--- sequence. Unfortunately, we have not yet identified unambiguously our predicted "stacked hexatic" liquid crystal with orientational long-range order but positional short-range order. The work on 40.8 has been published.<sup>5</sup>

References

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