

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 are currently implementing 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. COMMENSURATE-INCOMMENSURATE TRANSITION OF MONOLAYER KRYPTON ON GRAPHITE

We have carried out an x-ray scattering of the commensurate-incommensurate transitions (C.-I.T.) of monolayer krypton on the surface of ZXY exfoliated graphite at temperatures of 80.0 K and 89.3 K. At submonolayer densities the krypton has a $\sqrt{3} \times \sqrt{3}$ R 30° structure, commensurate with the graphite (0001) plane. As a function of chemical potential, and hence coverage, the krypton atoms move out of the $\sqrt{3} \times \sqrt{3}$ R 30° positions, forming a triangular lattice which is incommensurate with the substrate. We find¹ that (a) the transition appears to be second order with the simple power-law behavior $\epsilon \sim (\mu - \mu_c)^{1/3}$, (b) the transition occurs via the formation of a superlattice of domain walls, and (c) interesting and complicated line-shape phenomena occur near the transition. Current theories of the C.-I.T. are not adequate to describe these results.

2. STRUCTURE, PHASE DIAGRAM AND MELTING OF XENON ON GRAPHITE

The spacing of the xenon atoms in bulk xenon is intermediate between the 2×2 and $\sqrt{3} \times \sqrt{3}$ structures on graphite. This suggests that xenon might form an incommensurate lattice on graphite. We do indeed find that xenon forms a triangular lattice which is incommensurate except at low temperatures ($T < 65$ K) and high coverages. At higher temperatures where interesting thermodynamic phenomena occur, the system then functions as a model 2D continuous-symmetry solid. In our x-ray studies we find evidence for (i) the existence of a well-defined triple point as in 3D materials, (ii) a sharp nearly second-order melting transition, and (iii) novel coexistence phenomena at low coverages which indicate the importance of finite-size effects. Our analysis of the triple-point and coexistence experiments is complete and has been submitted for publication.² We are currently carrying out a detailed analysis of the melting data in order to make a quantitative comparison with current theories such as that proposed by Kosterlitz and Thouless.

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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 two of which are 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 structure, although the data are consistent with incommensurate successive layers. Work on this most interesting system is continuing.

4. STRUCTURE OF WELL-ORDERED SMECTIC PHASES

Smectic liquid crystals are conventionally defined as systems consisting of a one-dimensional density wave in a three-dimensional fluid. However, in many liquid crystals there are additional phases, conventionally labelled, SmB, D, E, F, G, and H with various degrees of order perpendicular to the density-wave direction. Further, existing x-ray evidence seems to indicate that this in-plane order often only extends a limited distance along the one-dimensional axis. As discussed in last year's report, we have constructed a simple model based on the Halperin-Nelson-Kosterlitz-Thouless theory of melting in 2 dimensions which appears to be able to account for the variety of phases suggested by the experiments. Most importantly, we identify

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a new 3D phase consisting of "stacked hexatics" — a system with long-range orientational order, but only short-range in-plane and between-plane positional order.³ We have now carried out a high-resolution x-ray study of the SmB phase of 4.0.8 which, according to existing data, appeared to be describable as the stacked hexatic phase. Unfortunately, our x-ray data show clearly that the SmB phase of 4.0.8 corresponds to an extremely soft solid.⁴ It now appears likely that most systems labelled as higher order smectics are, in fact, solids as we have found for 4.0.8. This is rather disappointing since our "stacked hexatic" phase would have represented a genuinely new phase of matter.

5. CRITICAL BEHAVIOR OF THE SmA-SmC TRANSITION OF $\bar{8}S5$

We have carried out measurements of the A-C transition in $\bar{8}S5$ in magnetic fields which are sufficiently large that the liquid-crystal director is held fixed in the SmC phase. Hence the SmA Bragg peak splits into a ring of scattering. The angular breadth of the ring gives the magnitude of the tilt-order parameter ϕ directly. One may also measure simultaneously the planar spacing d . We find to great precision $d_A - d_C \sim \phi^2$ and that ϕ exhibits mean-field behavior, that is, $\phi \sim (T_C - T)^{1/2}$, over the reduced temperature range $5 \times 10^{-3} > 1 - T/T_C > 3 \times 10^{-5}$. We have constructed a straightforward theory using the Ginzburg criterion which indicates that the true critical region should be unobservably small for most A-C transitions; this enables one to understand a large number of hitherto puzzling results in literature. These results have now been published.⁵

6. OBSERVATION OF ALGEBRAIC DECAY OF POSITIONAL ORDER IN A SMECTIC LIQUID CRYSTAL

A smectic-A liquid crystal in three dimensions has been predicted to exhibit algebraic decay of the layer correlations rather than true long-range order. As a consequence, the smectic Bragg peaks are expected to be power-law singularities of the form $q_{\parallel}^{-2+\eta}$ and $q_{\perp}^{-4+2\eta}$, where $\parallel(\perp)$ is along (perpendicular to) the smectic density-wave direction, rather than delta-function peaks. Observation of these phenomena requires very high instrumental resolution together with a resolution

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function with wings which drop off much more rapidly than $q_{\parallel}^{-2}(q_{\perp}^{-4})$. We show that these requirements may be met by using a three-crystal x-ray spectrometer with multiple-reflection channel-cut crystals as monochromator and analyzer. We find that the smectic-A Bragg peaks observed in the liquid crystals octyloxycyanobiphenyl are indeed consistent with the predicted power-law singularity form. Furthermore, the explicit values of η required to describe the measured profiles are in accordance with calculations of η using the harmonic approximation with empirically determined splay and layer compressibility elastic constants.⁶

References

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