

5. X-Ray Diffuse Scattering

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In this research program, modern x-ray scattering techniques are used to study the structures and phase transitions in novel states of condensed matter. We have two principal experimental facilities. At M.I.T. we have three high-resolution computer controlled x-ray spectrometers using either a conventional or high intensity rotating anode x-ray generator. 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 2 K and 500 K with a relative accuracy of $2 \times 10^{-3} \text{K}$. We are currently installing a two spectrometer system at the National Synchrotron Light Source at Brookhaven National Laboratory. This makes 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 opens up a new generation of experiments. Synchrotron x-ray scattering experiments are also carried out on a wiggler beam line at the Stanford Synchrotron Radiation Laboratory.

As part of this JSEP program we are designing and building an x-ray compatible high vacuum single crystal surface apparatus. This will enable us to use synchrotron radiation to study the structure and transitions occurring at single surfaces. The possibilities with this seem virtually unlimited. Our current experiments in this program are concentrated in two areas: (i) the growth, structure, and phase transitions of intercalant materials, most especially bromine-intercalated graphite, (ii) the structure and phase transitions of smectic liquid crystals.

5.1 Intercalation Compound Structures and Transitions

Intercalation compounds represent a family of materials in which a foreign species (e.g. Br_2) is inserted between the layers of a lamellar material such as graphite. If the intercalant enters every n th layer then the resultant material is referred to as a stage- n intercalation compound. We have initiated a program to study "in-situ", using high resolution x-ray scattering techniques, both the intercalation process itself and the structure and transitions of the intercalation compound as a function of

temperature, concentration, and stage index. Our initial work has concentrated on the system bromine-intercalated graphite $C_{7n}Br_2$.^{1,2}

The intercalate plane is found to have three sublattices and each sublattice has a centered ($\sqrt{3} \times 7$) rectangular structure with four Br_2 molecules per 2D unit cell in the commensurate phase. The coherently ordered in-plane bromine regions exceed 10,000 Å in size. In the stage-4 material a commensurate-incommensurate (CIT) transition is observed at $342.20 \pm 0.05^\circ K$. In the incommensurate phase, a stripe domain pattern becomes established in a single domain of a sublattice along the 7-fold direction. The incommensurability as a function of reduced temperature exhibits power law behavior with an exponent of 0.50 ± 0.02 confirming existing theories. The relative shifts observed for the various harmonics are accurately predicted by a sharp domain wall with $4\pi/7$ phase shifts. A power-law lineshape reflecting the lack of true long range order is observed for the incommensurate intercalant layer, yielding values for the exponent η consistent with model calculations. The intercalate layer exhibits a continuous melting transition from a two-dimensional solid phase to a smectic liquid crystal phase, occurring at $373.41 \pm 0.10^\circ K$ for a stage-4 compound.

We are continuing these detailed studies for lower stage material; we have also carried out some initial experiments on graphite intercalated with potassium and mercury. This system exhibits superconductivity at 1 K and thus is of particular interest.

5.2 Smectic Liquid Crystals

Liquid crystals are made up of rod-like molecules. In the nematic phase the axes of the molecules align parallel to each other but the centers of mass of the molecules are still randomly distributed so that one has a pure fluid structure factor. In the smectic A and C phases a one-dimensional sinusoidal density wave is set up either along (A) or at an angle (C) to the molecular axis. Thus, these smectics are like solids in one direction and fluids in the other two. These systems exhibit particularly interesting phase transitions which present an important challenge to modern theories of critical phenomena. At lower temperatures many liquid crystal materials exhibit more ordered phases such as smectic B, F, and G. These have well-developed in-plane triangular order. If the order is truly long range then the phase is a plastic crystal. Otherwise, the smectic may be a realization of a novel phase of matter labelled a "stacked hexatic" with long range order in the crystalline axes but only short range order in the positions of the molecules. We have recently studied in some detail the smectic phases and phase transitions in two related materials, heptyloxybenzylidene-heptylaniline (70.7)³ and butyloxybenzylidene-heptylaniline (40.7).⁴

Our work in 70.7 has concentrated primarily on the B-phase. We have carried out an x-ray diffraction study using both rotating anode and synchrotron sources of structures and restacking transitions within the B phases. The system evolves from a hexagonal close-packed structure, through intermediate orthorhombic and monoclinic phases, to a simple hexagonal structure. The

monoclinic phase has a temperature-dependent shear which transforms the system from orthorhombic to hexagonal. The latter three phases exhibit a single- \vec{q} sinusoidal modulation of the molecular layers. The sinusoidal modulation is believed to represent a precursor to the tilted (G) phase at lower temperatures. This behavior is much richer than anyone had previously considered possible within the B-phase. The experiments demonstrate most clearly that there is need for a significant development of theories for the structures of quasi-2D molecular solids.

In 40.7 we have carried out an encyclopaedic study of all of the liquid crystal phases and phase transitions. Here we emphasize our results for the smectic A – smectic C transition. This is a second order transition in which the molecular axis spontaneously tilts with respect to the density wave direction. This transition would appear to be the simplest liquid crystal phase change; in spite of that, it has been the subject of considerable controversy in the literature.

In our previous JSEP work we have argued, using a Landau theory and the Ginzburg criterion, that A–C transitions should exhibit mean field behavior over the temperature range accessible by current experimental techniques. However, if interpreted naively, recent measurements in two materials, butyloxybenzylidene–heptylaniline (40.7) and azoxy–4, 4'–di–undecyl– α –methylcinnamate (AMC–11), seem to contradict this prediction. Specifically, over the reduced range 5×10^{-3} to 5×10^{-5} in both cases the tilt follows a power law with $\beta \simeq 0.36$; that is, these materials seem to exhibit helium-like critical behavior. By carrying out order parameter, heat capacity and light scattering measurements we have found that the data are uniquely described by mean field theory with an unusually large sixth order term. The measured $\beta = .36$ thus represents a crossover from $\beta = 1/2$ to $1/4$ regimes demonstrating that the original Ginzburg criterion arguments are correct. We do not, however, have a plausible microscopic explanation for the large sixth order term.

References

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