

## 8. X-Ray Diffuse Scattering

### Academic and Research Staff

*Prof. R.J. Birgeneau, Dr. A.R. Kortan, Dr. M. Sutton, Dr. J.W. Chung*

### Graduate Students

*K. Evans-Lutterodt, H. Hong, A. Mak, L.J. Martinez-Miranda, S.G.J. Mochrie,  
B.M. Ocko, E. Specht*

*Joint Services Electronics Program (Contract DAAG29-83-K-0003)*

*Robert J. Birgeneau*

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 the 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 single surfaces; such experiments are now being initiated. Our current experiments in this program are concentrated in three areas: (i) the growth, structure and phase transitions of intercalant materials, (ii) the structure and phase transitions of smectic liquid crystals, (iii) the phases and phase transitions of rare gas atom monolayer and bilayer films on graphite.

### 8.1 Intercalation Compound Structures and Transitions

Intercalation compounds represent a family of materials in which a foreign species (e.g.,  $\text{Br}_2$ ) 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. In this program we study both the intercalation process itself and the structure and transitions of the intercalation compound as a function of temperature, concentration, and stage index. Our

current work is concentrated on the systems bromine-intercalated graphite  $C_{7n}Br_2^{-1}$  and  $SbCl_5$ -intercalated graphite.<sup>2</sup>

In bromine-intercalated graphite, 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 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. For this phase, current theory predicts that the superlattice peaks should be power law singularities of the form  $(Q - Q_n)^{-2+x_n}$  where  $x_n = \frac{2n^2}{49}$  and  $n$  is the order of the harmonic. To probe these line-shape effects we have carried out a high resolution synchrotron study of a sample of  $C_{28}Br_2$  grown "in situ". Dramatic changes are indeed seen in the intensities and shapes of the successive harmonic peaks. Quantitative analysis shows that the first five harmonics are indeed well-described by the above form; further,  $x_n$  is given by  $2n^2/49$  to an accuracy of about 20%. We also confirm that the line-shape is independent of the domain wall separation.

We have also carried out a combined x-ray diffraction and electron diffraction study of  $SbCl_5$ -intercalated graphite.<sup>2</sup> We have examined both single crystal and microcrystalline powder samples using the two different techniques. With x-ray diffraction we find a single phase, commensurate  $\sqrt{7} \times \sqrt{7}$  structure which is stable between room-temperature and 16 K. On the other hand, initial electron diffraction measurements showed a crystal  $\rightarrow$  glass transition at about 200 K for the intercalant on decreasing temperature, in agreement with earlier studies. By a careful study of the behavior as a function of electron beam current and energy, we find that the glass transition is driven by the electron beam. Below  $\sim 150$  K the fluence required to drive the transition exhibits an activation energy of  $\sim 0.01$  eV while above 150 K the activation energy increases dramatically to  $\sim 0.1$  eV. We are currently analyzing various models for this novel behavior. A quasi-two dimensional glass with controllable disorder should be of much general interest.

## 8.2 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, G, and I. 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 are continuing to study in some detail the smectic phases and phase transitions in a number of materials. Special emphasis has been given to nematic–smectic A–smectic C multicritical behavior.

The thermotropic liquid crystal material pentylbenzenethioheptyloxybenzoate (*755*) exhibits an N–S<sub>c</sub> transition at ~40°C. However, we have found that addition of a few mole percent octyloxycyanobiphenyl (80CB) changes the sequence of phases to  $N \rightarrow S_A \rightarrow S_C$  with decreasing temperature. By careful study of the transitions in a series of mixtures, we find that there is a triple point, labelled the NAC multicritical point, at which the three phases come together. This NAC point has been the subject of extensive theoretical and experimental investigation; the principal motivation for this interest is that in some models the NAC point is a Lifshitz transition; this is a special multicritical point at which the coefficient of the gradient term in the Landau–Ginsburg expansion is exactly zero. We have studied the nematic and smectic mass density structure functions in a series of mixtures around the NAC point. We find S<sub>A</sub>-like fluctuations, that is fluctuations with a positive  $q^2$  coefficient, throughout most of the nematic phase. However, near the N–S<sub>c</sub> boundary there is indeed a line, emerging from the NAC point, along which the  $q^2$  coefficient vanishes. The gradient-squared coefficient is negative between this line and the N–S<sub>c</sub> boundary. This provides a dramatic confirmation of the Lifshitz concept. However, the detailed geometry of the phase boundaries and the Lifshitz line remain to be explained. We are currently analyzing these data quantitatively.

### 8.3 Structures and Transitions of Monolayer Rare Gas Crystals

The phases and phase transitions of monolayer films of rare gases physisorbed onto the basal planes of graphite continue to be the subject of active research. They provide model examples of two dimensional freezing and of transitions driven by competing period effects — both subjects of considerable controversy. The principal advantages of the rare gas–graphite systems for addressing these issues are that, first, the interactions are simple and well known so that first principle's calculations are possible and second, a broad range of sophisticated experiments, carried out in thermal equilibrium, are feasible. In the past year we have used synchrotron radiation to probe the freezing of submonolayer films of xenon on graphite and to study a novel transition in which a krypton monolayer spontaneously rotates with respect to the graphite substrate.

The xenon freezing experiments were carried out using both ZYX graphite,<sup>3</sup> an azimuthal powder, and an exfoliated single crystal<sup>4</sup> as substrates. The latter provides orientational as well as positional information. Both experiments show that the incommensurate xenon freezing transition is continuous for coverages as low as 0.9 monolayers; further, at lower coverages

where the transition appears to be first order the fluid is very well correlated. These experiments demonstrate, in agreement with our original studies at 1.1 layers, that the fluid correlation length reaches at least 200 Å before the solid appears for freezing temperatures as low as 125 K. From the exfoliated single crystal studies we find that the angular width of the fluid diffraction spots scales linearly with the radial width. This is the behavior expected for a "hexatic" fluid as predicted by Halperin and Nelson. Unfortunately, because of our lack of knowledge of the substrate orienting field we cannot make a definitive statement about the existence of a hexatic phase in the absence of a substrate. Certainly we see no remnant of the hexatic-isotropic transition expected for a substrate-free hexatic fluid.

Several years ago, Shiba made the interesting prediction that an incommensurate overlayer would exhibit a continuous transition from an aligned to a rotated phase as a function of lattice mismatch. The transition occurs as a result of a crossover from the non-linear to the linear modulation regimes. Further, Shiba calculated quantitatively the expected rotation angle versus lattice mismatch for a given interaction potential ratio. Krypton on graphite turns out to provide a very good illustration of this effect. In order to probe this we have used an improved sample cell developed by K. D'Amico to allow for single crystal studies. We find that at ~82 K an aligned-rotated transition does indeed occur for a lattice mismatch of ~3.5%; this threshold value corresponds to a domain wall half-width of about three lattice constants. Shiba's theory is found to describe our data quantitatively.<sup>5</sup>

#### References

1. S.G.J. Mochrie, A.R. Kortan, R.J. Birgeneau, and P.M. Horn, *Phys. Rev. Lett.* **53**, 985 (1984).
2. G. Roth, L. Salamanca-Riba, A.R. Kortan, G. Dresselhaus, and R.J. Birgeneau, submitted for publication.
3. P. Dimon, P.M. Horn, M. Sutton, R.F. Birgeneau, and D.E. Moncton, *Phys. Rev.* **B31**, 437 (1985).
4. S.E. Nagler, P.M. Horn, T.F. Rosenbaum, R.J. Birgeneau, M. Sutton, S.G.J. Mochrie, D.E. Moncton, and R. Clarke, *Phys. Rev. B.*, in press.
5. K.L. D'Amico, D.E. Moncton, E.D. Specht, R.J. Birgeneau, S.E. Nagler, and P.M. Horn, *Phys. Rev. Lett.* **53**, 2250 (1984).