

9. 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 two high-resolution computer controlled x-ray spectrometers using a high intensity rotating anode x-ray generator. Two more spectrometers are currently under development. 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 also have, in collaboration with IBM, 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 in turn has opened up a new generation of experiments. This facility is under continuous development to improve the optics and spectrometers. 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 metal and semiconductor surfaces and surface overlayers.

9.1 Intercalation Compound Structures and Transitions

Intercalation compounds represent a family of materials in which a foreign species (e.g., B_r) 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 system bromine–intercalated graphite $C_{7n}Br_2$.¹

Bromine–intercalated graphite has turned out to be an interesting model two dimensional system. Above 69.3° C the bromine has a novel structure in which it is in–registry with the graphite in one direction and out of registry or incommensurate in the other. This is referred to as a stripe–domain structure. One of the unusual features of such a structure, which we have characterized thoroughly,¹ is that in a diffraction pattern there are no true Bragg peaks. Rather the diffraction is characterized by power law singularities, $(Q-Q_n)^{-2+\eta_n}$, where the exponent η_n depends on the order (n) of the harmonic. Here the η_n are predicted exactly by theory. One of the interesting questions which had not been addressed quantitatively to date is how such a solid melts. Qualitatively, it is expected that one could have a continuous melting transition in which the bromine melts while the graphite stays crystalline. Further, on universality grounds it is expected that such a transition, if continuous, would be isomorphous to the superfluid transition in two–dimensional helium which is well described by a theory due to Kosterlitz and Thouless – a dramatic theoretical prediction. We have used high resolution x–ray synchrotron techniques to study this melting transition. A high quality single crystal of stage–8 bromine intercalated graphite was grown *in situ* on the x–ray spectrometer. The data from this experiment are still being analyzed. We find strong evidence for a sharp but continuous melting transition for the bromine. However, the liquid structure–factor in the well–correlated fluid phase is anomalous. Specifically, it does not seem to fit into the Kosterlitz–Thouless picture. We are continuing our analysis in an attempt to determine the appropriate description of this novel melting phenomenon.

9.2 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. One of the important issues in this field has been the critical behavior of the

nematic–smectic A transition. This might be viewed as the simplest melting transition in nature. In nearly all cases in studies of phase transitions one finds that the critical behavior is independent of the details of the system. For the N -problem, however, the exponents characterizing the transition vary from system to system. In order to elucidate this unusual phenomenon we have carried out a systematic study of the N - A transition² in two series of compounds: alkylbenzoate (nCB) and thiosulphate (\bar{n} S5). Here the aliphatic chain length $n(C_nH_{2n+1})$ may be varied continuously by making appropriate mixtures. We find that as one increases n in both series the exponents evolve continuously from $\Upsilon = 1.5$, $\nu_{\parallel} \simeq 0.80$ and $\nu_{\perp} \simeq 0.67$ to $\Upsilon = 1.1$, $\nu_{\parallel} = 0.6$ and $\nu_{\perp} = 0.5$; the latter are attained at the point where the transition changes from being second order to first order; as such, this point is a tricritical point and indeed the measured exponents are close to the predicted theoretical values for a tricritical point. We conclude therefore that the varied exponents reported in the literature for other systems simply reflect a crossover from critical to tricritical behavior.

As noted above, one of the most novel phases of matter occurring in the liquid crystal family is the "stacked hexatic." We have initiated synchrotron x-ray studies of free standing films of the material methylbutylphenyloctyloxybiphenylcarboxylate (8OSI) which is believed to exhibit a stacked hexatic phase in which the molecules are tilted with respect to the layer normal; this is labeled smectic I; at $\sim 78^\circ$ C with increasing temperature the S_I exhibits a transition into an S_C phase. Our initial measurements are very promising. We find that by applying a small field via $SmCo_5$ magnets one can orient the molecules and this, in turn, fixes the hexatic axes in the S_I phase. Thus we have produced the first single-domain sample in a liquid crystal hexatic; this makes quantitative studies of the relevant order parameters and densities possible. Currently we are studying the thermal evolution of the orientational and positional order throughout the C and I phases. Once these measurements are concluded we will begin studies in very thin films – 2 to 10 molecules thick.

9.3 Structures and Transitions in Two Dimensional Solids

As is now well-recognized, surface systems provide interesting examples of two dimensional phases and phase transitions. There are many different categories including pristine surface reconstruction, chemically adsorbed surface overlayers and physically adsorbed layers. Rare gases on graphite provide the best studied examples of this third category. Much of our surface science research program in the past several years has concentrated on the physics of monolayer krypton and xenon on graphite. The principal advantages of the rare gas-graphite systems 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.³ In the past year we have used synchrotron radiation to probe the freezing of submonolayer films of xenon on single crystal graphite.⁴

The single crystal substrate experiment allows one to study the evolution of the fluid correlation

length up to distances approaching a micron. This is unprecedented in surface structural studies. Our experiments were carried out for a coverage of 0.92 xenon monolayers at freezing. We find that the fluid correlation length evolves continuously up to at least 2000 Å before the solid phase is entered.⁴ 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.

We are continuing to develop our "chemically-active" single crystal apparatus. We expect to initiate synchrotron radiation studies of molybdenum surfaces in the spring of 1986.

References

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