

9.0 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 four high-resolution computer-controlled x-ray spectrometers using high intensity rotating anode x-ray generators. 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 2K and 500K 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. A third beam line designed to operate at short wave lengths is currently under development. These make 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.

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 a single surface; the first generation of such experiments has now been performed. Our current experiments in this program are concentrated in three areas: 1) the phases and phase transitions of metal and semiconductor surfaces and surface overlayers; 2) the structure and phase transitions of smectic liquid crystals; and 3) the growth, structure and phase transitions of intercalant materials.

9.1 Single Crystal Surface Studies

As noted above, x-ray synchrotron sources provide sufficient flux that it is possible to carry out high resolution diffraction studies of a single monolayer. In the past year we have studied three different systems: 1) monolayer xenon on graphite; 2) tungsten (100) with either oxygen or hydrogen adsorbed on the surface; and 3) pristine silver (110) as a function of temperature.

The xenon-on-graphite experiments represented a considerable technical advance on previous surface overlayer experiments. We used a single crystal of graphite with a mosaicity of 0.01° full-width-at-half-maximum (FWHM). This corresponds to a real space resolution of ~ 2 microns. The xenon coverage was accurately controlled using

a vermicular graphite ballast adjacent to the single crystal sample. We find that for a broad range of coverages, ~ 9 to 1.2 monolayers, with decreasing temperature the xenon exhibits the sequence of structures: aligned hexagonal incommensurate \rightarrow rotated hexagonal incommensurate \rightarrow aligned hexagonal incommensurate $\rightarrow \sqrt{3} \times \sqrt{3}$ $R30^\circ$ commensurate. The first and third transitions are first order while the second is continuous. The incommensurate-commensurate transition is similar to that exhibited by monolayer krypton on graphite with a $1/3$ power-law behavior; however, for xenon this power law is pre-empted by a first order transition at 1% incommensurability. From the data it is possible to deduce precise information about the surface potential and thereby to assess first principle's theoretical predictions for this model surface system.

From low energy electron diffraction studies it is known that tungsten (100) exhibits a variety of interesting surface phases when either oxygen or hydrogen is adsorbed onto the surface. We have used high resolution synchrotron radiation to study the surface oxygenation and hydrogenation processes. Because of the extreme reactivity of the tungsten surface, these experiments are technically quite difficult. We have, nevertheless, managed to observe both the saturated oxygen overlayer structure, which has a simple 2×2 symmetry, and various other chemisorbed phases. These data are still being analyzed. Quite fascinating results are obtained with the absorption of hydrogen. For about 0.2 monolayers of hydrogen, a centered 2×2 structure forms; we observe intense x-ray diffraction from this phase at room temperature. This necessitates that there is considerable movement of the tungsten surface atoms in the formation of the 2×2 structure. With increasing hydrogen coverage a commensurate-incommensurate transition occurs. These data are currently being analyzed.

Surface roughening is a novel phenomenon which has been extensively investigated theoretically and by computer simulation. However, there have been only limited experimental investigations in real materials. Recent atom beam scattering experiments have suggested that low index metal surfaces may show a reversible roughening transition. We have carried out a detailed study of the Ag (110) surface. We find that at about 400°C the Ag (110) surface indeed becomes rough and by $\sim 600^\circ$ the surface is sufficiently disordered that it no longer gives a clear diffraction signal. Remarkably, as the sample is cooled, the surface reforms reversibly recovering its original form at room temperature. The data from this experiment are currently being analyzed.

9.2 Structure and Phase Transitions of Smectic Liquid Crystals

The mechanism by which crystalline order is established as a fluid freezes is still an unsolved problem. In liquid crystal materials, the freezing process may occur in several steps. Each step may be thought of as the freezing out of some particular type of random motion or disorder as the system cools. Choosing the orientation in space of the axes of the crystalline lattice is one of the crucial steps necessary for the establishment of crystalline order. In most physical systems, this choice of orientation occurs simultaneously with the establishment of a true spatially periodic crystal lattice. However, there is no reason why the two processes must occur simultaneously. The logical possibility that a phase of matter might have a well defined orientation for the crystal axes without having actually established the lattice has been recognized for 50 years. These strange phases of matter are called Bond Orientationally (BO) ordered to indicate that

it is the orientation of the bonds between nearest neighbors, not the distance between nearest neighbors, which is becoming fixed.

The suggestion that several of the unusual liquid crystal phases might be physical realizations of BO ordered phases was made several years ago. However, samples of high enough quality and x-ray scattering equipment with high enough intensity at high resolution were not readily available. The sample problems were solved by the development of freely suspended film techniques of liquid crystal at Harvard, Bell Labs and MIT. The development of high resolution x-ray scattering apparatus on synchrotron x-ray sources has solved the latter obstacle.

The signature of a BO ordered phase in an x-ray scattering experiment is a periodic variation in the scattered intensity while rotating the lattice. We therefore performed a series of such angular scans as the sample was cooled through the putative hexatic phase transition. At high temperatures the scan is flat to within our counting statistics. As the sample is cooled, a measurable modulation develops. Further cooling causes the slight modulation to grow into definite peaks, one every 60° .

Taking advantage of this extremely high quality data taken at NSLS, we performed a detailed line-shape analysis. The analysis led to the empirical discovery of mathematical scaling relations describing the growth of the BO order. Motivated by this discovery, a theoretical model was developed which explains the growth of BO order based only on the underlying symmetry of the physical system. Since the model applies to any physical system with the appropriate symmetry, it is applicable to a wide variety of theoretical and experimental systems. Using our model we can describe exactly how the orientation of the crystal lattice develops with temperature without any knowledge of the details of the system other than its symmetry.

9.3 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. 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, is that in a diffraction pattern there are no true Bragg peaks. Rather, the diffraction is characterized by power law singularities, $(Q - Q_n)^{-2 + \nu_n}$, where the exponent ν_n depends on the order (n) of the harmonic. Here the ν_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.

Our results show a number of striking features: (1) the transition is indeed continuous, at least for length scales varying from several thousand Angstroms to fifty Angstroms; (2) higher harmonics of the mass density wave vanish successively as the temperature is raised. Thus, even though from the peak positions we know that the domain walls remain microscopically sharp, the order parameter acquires a sine-wave character; (3) the transition is very rapid, with the primary evolution in the structure factor occurring within 1°C; (4) the aspect ratio of the scattering changes through the transition; and (5) the detailed nature of the correlations is unusual in that a power-law description of $S(\vec{Q})$ works throughout the temperature range studied; that is, the anticipated crossover from algebraic to exponential decay of the positional correlations at $\eta_1 = 1/4$ does not seem to occur.

We have also carried out a combined electron and x-ray diffraction of SbCl_5 intercalated graphite. Of particular interest is the unusual commensurate $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ to glass "phase change" (C-G) in the intercalate layer that has been observed to take place on cooling below $\sim 180\text{K}$ using TEM, where the low-temperature phase is the glass phase. The C-G phase change is not observed in x-ray diffraction experiments. It was first suggested that the C-G phase change reported for stages 1-4 occurred only in dilute samples, and that further the intercalate layer was dilute in the thin samples needed for TEM, but not in the thick samples used in x-ray diffraction. In order to determine whether the discrepancy between the x-ray and TEM results was due to differences in sample composition or to differences in the experimental techniques, we performed x-ray diffraction and electron microscopy studies at low temperatures using stage-2 SbCl_5 -CIG samples of common origin for both types of experiments. We investigated the dependence of the C-G phase change on host material, host crystallite size and experimental technique. We find from x-ray and electron diffraction experiments performed on stage-2 SbCl_5 -GIC samples that the crystalline to glass-phase change results from electron-beam damage. Two competing annealing processes are observed with two different activation energies. This crystalline-glass phase change is the result of damage attributed to atomic displacements indirectly induced by electron beam irradiation. We have devised a model for the damage process that induces the C-G phase change. The model is supported by a computer image simulation of the commensurate $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ phase.

Publications

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