STRUCTURE AND DYNAMICS IN LOW-DIMENSIONAL GUEST-HOST SYSTEMS

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I. INTRODUCTION

New synthetic materials continue to be discovered at a rapid rate. Many of these can be broadly described as *guest-host systems*, in the sense that a range of compositions is accessible by selectively inserting heteroatoms or molecules into the interstitial sites in an otherwise pure starting material. The premier examples are layer intercalates (graphite, transition metal di- and trichalcogenides, silicate clays) and doped polymers (notably polyacetylene). With a somewhat broader definition of intercalation, one might include the high- T_c cuprate superconductors (variable oxygen and alkaline earth concentrations), ion-exchanged beta-alumina and related defect oxides, and alkali metal-doped buckminsterfullerene (C_{60}). The interest in these material families for energy applications is directly attributable to the guest-in-a-host feature, either by exploiting guest ion mobility in electrochemical devices or by tuning/optimizing properties via control of guest concentration and sublattice structure.

It is becoming increasingly apparent that great advantages are to be gained by considering these classes of complex materials globally, as an alternative to focussing on one family at a time. Important examples of beautiful unifying themes have been identified in some cases, and these are ripe for further exploitation. Our work in the '70's on graphite intercalation compounds evolved naturally into related experiments on transition metal dichalcogenide intercalates and doped polyacetylene. This background in guest-host systems enabled us to make a major impact on the new field of "buckyball" materials and their doped derivatives. (A brief foray into cuprates was not enormously useful and has been dropped.)

This proposal is for a 3-year renewal of the current grant of the same title, DE-FG02-86ER45254, for which \$ 827,568 has been awarded over the 6-year period 6/1/86 - 5/31/92. Part II of this document is a progress report covering the first 25 months (6/89 to 7/91) of the present 3-year period. Part IV describes the proposed research 6/1/92 - 5/31/95. Selected reprints and manuscripts in process are attached as appendices.

II. HIGHLIGHTS OF CURRENT GRANT

A. PREAMBLE

From the previous 3-year renewal proposal, written in mid-1988:

"..... Research on these materials has proceeded independently, with little effort devoted to exploring their commonalities. It has been amply demonstrated that they all exhibit unusual features in their static crystal structures, lattice vibrational properties and/or guest diffusion dynamics. It thus seems evident that opportunities exist to transfer knowledge from the more mature subfields to the newer ones, in order to address crucial problems in structure and dynamics....."

".... We have been active since 1975 in the study of graphite intercalation compounds, in which the most dramatic structural feature is the staging phenomenon - a sequence of 1-D superlattices of alternating host and guest layers whose periodicity and perfection vary with all the thermodynamic variables. Staging is thus intimately involved in the above issues. Major progress has been made in the (previous) grant period in understanding staging in terms of competing interactions (inter- vs. intralayer, guest-guest vs. guest-host etc.), to the extent that a unifying microscopic picture is emerging....."

"The principal experimental tools are x-ray and neutron scattering, using in-house facilities, the HFBR and NSLS at Brookhaven, and the ILL in Grenoble as appropriate. (We are making a conscious effort to increase the supply of PhD's trained in neutron scattering.) Sample materials are either grown in-house or provided through collaborations with other groups."

B. GRAPHITE INTERCALATION COMPOUNDS

1. Structure and Dynamics in C_8AsF_5

We used elastic, inelastic and quasielastic neutron scattering to study the temperature-dependent structure and dynamics in the prototype stage-1 acceptor compound C_8AsF_5 . It is well-known that AsF_5 dissociates upon intercalation; the diversity of constituents in the intercalate layer guarantees a rich but complex phase diagram. Hendricks-Teller broadening of (00L) profiles indicate a tendency to form stage-2 galleries at low T, so the average out-of-plane intercalate density must decrease with decreasing T. The implied converse dependence of in-plane density is revealed in a complicated sequence of ordered in-plane structures, one of which becomes denser with decreasing T but never locks in to the graphite periodicity. Some of the molecular motions are slow enough (even at low T) to observe quasi-elastic line broadening (or QENS) with our triple-axis spectrometer. Unlike the alkali GIC's, we see no finite-energy peaks associated with discrete intercalate-derived phonon modes, not even down to 10K. The Q-dependence of the quasi-elastic width exhibits structure on top of an overall Q^2 dependence. We associate the latter with free-particle molecular diffusion, while the structure is likely due to jump diffusion or rotation.

2. Jump Diffusion and Phonon DOS in Stage-2 Li-GIC's

In this project we exploited the different in-plane densities and T-dependent structures of LiC_{12} and LiC_{16} to study jump diffusion and in-plane phonon spectra versus stage and long- and short-range order, taking the LiC_6 results as a point of departure. We found no QENS in LiC_{12} for $T < T_m = 500K$, while the T-dependent quasielastic broadening energy $\Gamma(Q)$ for LiC_{16} is consistent with nearest-hexagon jumps by incoherent scatterers over a barrier 0.55 eV, half the value obtained in the ordered phase of LiC_6 .

For $T > 500K$, LiC_{12} is dilute stage-1 while LiC_{16} is less-dilute stage-2; surprisingly, both $\Gamma(Q)$'s imply a jump vector L close to $4.92 \text{ \AA}$ (third-neighbor sites) and a much smaller barrier energy. A jump vector this long is highly unlikely since essentially all the sites are accessible to a jump-diffusing particle in both compounds. We suspect that this inconsistency results from the use of oversimplified models for the QENS broadening, either the neglect of spatial and temporal correlations in the jump process itself, or the assumption that the QENS is dominated by incoherent scattering from Li. Q-integrated inelastic spectra reveal structure in the phonon DOS which disappears above T_m in LiC_{12} ; the heavy alkali analogs (e.g. RbC_{24}) behave quite differently, presumably due to a domain-discommensuration lattice which characterizes the low-T ordered phase of heavy alkali compounds.

C. STAGING TRANSITIONS IN LI- AND Ag-TiS₂

Graphite intercalation compounds transform at high pressure to higher stages with greater in-plane densities. These transformations are driven by local elastic distortions which favor the creation of dense islands, which in turn correlate in the c-direction to give well-ordered staging superlattices. The entire process can be modelled in a continuum theory which accounts for the host layer elastic properties. The pressure response using different intercalates depends only on the c-axis component of the local distortion since the in-plane "healing length" is purely a property of the host layers. Other groups have developed generic continuum models for elastic interactions, the implication being that staging transitions for any intercalate in any host lattice may be thus analyzed merely by scaling to the intercalate size and the host layer bending modulus.

Our results on ITMD's show that the continuum approach breaks down for moderately stiff host lattices. Dilute stage-1 $Li_{0.5}TiS_2$ remains stage-1 up to 55 kbar while a similar Ag compound exhibits a combined staging/polytype transition at very low pressure. It is difficult to reconcile a large difference in threshold pressures within the continuum model, since the healing length (which controls the magnitude of the in-plane attractive interaction) is independent of the intercalate radius. On the other hand, our results can be rationalized by accounting for the different intercalate radii compared to the volume of a tetrahedral interstitial site. Li is small enough that a reduction in specific density per intercalate with increasing pressure is not required. The c-axis strain can easily be accommodated just by compressing the van der Waals gallery. Li easily "hides" in the interstitial site up to a predicted pressure of 70 kbar, at which point a further volume reduction requires creation of dense islands and empty regions. On the other hand, Ag^+ completely fills the tetrahedral interstices already at 1 atm., thus the phase transition begins at very low P (see Appendix A).

D. STRUCTURE AND DYNAMICS OF CONDUCTING POLYMERS

1. Staging in Doped Polymers

In principle the low-T dilute phases in these materials should consist of 2D superlattices of fully-occupied 1D channels, analogous to the 1D layer sequences ("stages") of densely-filled 2D galleries in GIC's. We previously calculated a mean-field phase diagram *a la* Safran, mainly as a guide to the experiments. Using *in situ* x-ray diffraction and electrochemical doping, we found two stages in $[(CH)_y]_x$ with y (or V_{oc}) as independent variable. The results confirm directly for the first time that anomalies in macroscopic quantities vs. V_{oc} do indeed signal first-order structural transitions. Detailed analysis shows that the polymer chain setting angle goes through several stepwise rotations as the channels are "prepared" to accept the alkali intercalant (see Appendix B).

2. Broken Symmetry Intercalation Lattices

The lattice symmetry of polymer intercalation compounds depends fundamentally upon the size of the intercalate, unlike the 1-D staging structures in layer intercalates. In particular, the formation of quasi-1D dopant channels imposes rotations of the host chains about their long axes such that small alkalis (Li, Na) induce a triangular superlattice while large alkalis (K, Rb, Cs) force larger channels with square 2D symmetry. We have performed detailed analysis of high-quality x-ray diffraction measurements on K-doped $(CH)_x$ and Cs-doped (poly)paraphenylene-vinylene (PPV) which demonstrate that the simple symmetries previously assumed are broken by rotations and translations of the polymer chains, presumably originating in some new interchain interactions. Steric arguments can be applied to predict similar phenomena in other systems, with implications for both the phase diagrams and 3-D band structure calculations. This topic is being studied in collaboration with Prof. M. Winokur, U. Wisconsin (see Appendix C).

3. Structure and Dynamics in Cs-doped Polyacetylene

The x-ray profile of heavily doped $[(CH)Cs_y]_x$ was analyzed on the basis of three-dimensionally ordered intercalate channels. Fifteen peaks representing 27 unique reflections are well-represented (positions and intensities) by a tetragonal pseudo-cell with $a = b = 9.093 \text{ \AA}$, $c = 7.950 \text{ \AA}$ containing 24 (CH) and 4 Cs units ($y = 0.167$). The Cs and (CH) sublattices are actually incommensurate along c , with 6.46 undistorted (CH) units per Cs implying $y = 0.15$. Reflections with non-zero L are significantly less intense than calculated neglecting the Debye-Waller factor, indicating large amplitude c -axis thermal motion of Cs ions. The fractional linear in-plane dilation upon replacing K with Cs is within 20% of the corresponding value in graphite intercalates (see Appendix D).

4. Conductivity and Cell Potential in $[(CH)K_y]_x$

A high-resolution quasi-equilibrium *in situ* study of electrical conductivity and open circuit voltage V_{oc} during potassium doping and dedoping of an oriented $(CH)_x$ electrode has been performed. The goal was to identify anomalies which might be associated with subtle structural transitions, in order to guide future detailed x-ray experiments. Features in dV_{oc}/dy and $d\sigma/dy$ ($y = K$ mole fraction) found previously at $y = 0.06, 0.12$ and 0.15 were confirmed and correlated with recent x-ray and esr results and with a model of staging via intercalation channels. We also found new features at $y = 0.03$ and 0.08 , the former coinciding with a similar esr feature. We propose that these are signatures of structural effects which do not involve major changes in lattice constants or unit cell symmetries. We tentatively assign the $y = 0.03$ feature to a metastable "dilute stage-2" structure by analogy to graphite intercalates. Three phases with the same stage-1 channel structure are inferred from the observation of three plateaus in $V_{oc}(y)$ in the range $0.10 < y < 0.17$ upon dedoping. A maximum $\sigma = 17500 \text{ S/cm}$ is found near $y = 0.12$ during the first doping cycle. After successive cycles σ_{max} decreases, the maximum attainable y also decreases, and the overall form of V_{oc} vs. y approaches the ideal behavior for an intercalation electrode exhibiting first-order phase transitions (see Appendix E).

5. Polarized Vibrational Density of States

It is now well-established that the novel physics of conjugated polymers results from strong electron-phonon and/or electron-electron interactions. The conceptual state-of-the-art is the Su-Schrieffer-Heeger Hamiltonian, which treats electron-phonon coupling within a single chain at the level of BCS theory - a single empirical number akin to the MacMillan λ parameterizes the whole problem. Now that the importance of 3-D effects is becoming important, one

would like to have a better model which incorporates the actual phonon spectrum and includes inter-chain vibrational modes.

Experimental results on vibrations are limited to a few zone-center intrachain modes (Raman, IR); theorists have yet to attempt a 3-D lattice dynamics calculation. More detailed experiments are frustrated by the limited quality and quantity of available samples - a complete phonon dispersion study via coherent inelastic neutron scattering would require several grams of deuterated material with a c-axis mosaic at least twice as good as the best available. As a first step towards this ultimate goal, we have developed a technique to obtain polarized densities of vibrational states from incoherent inelastic neutron scattering. In this technique the finite mosaic is exploited to Q-integrate the energy-dependent scattering from hydrogen motions. A simple rotation of the sample allows to separate the two principal polarizations, which gives for the first time information about inter-chain vibrations and 3-D effects.

A first 4-day run at the Institut Laue-Langevin reactor yielded results for polyacetylene and polyaniline at several temperatures. We proved the validity of the technique by verifying the polarization of previously-known modes. More importantly, we identified a number of new features, in particular a mode at 3 meV polarized along the chains. The best candidate for this very soft mode is the out-of-phase longitudinal motion of the two inequivalent chains/cell. This mode will be very sensitive to changes in interchain interactions with doping, and may also serve as a rather direct probe of topological defects (solitons, polarons). Analysis of polyaniline data (in progress) shows a mode at 12 meV which may turn out to be the ring torsion mode responsible for thermochromism (see Appendix F).

6. Crystal Structure of *trans*-Polyacetylene Revisited

New x-ray diffraction data on high-quality *trans*-(CH)_x shows that the bond alternation is out of phase on adjacent chains, and therefore the correct space group is $P2_1/n$. Previous attempts to resolve this question by analyzing only the (00L) intensities have yielded ambiguous results; all of the previously-published diffraction experiments show some (001) intensity which is not allowed in $P2_1/n$. By analyzing individual off-axis peak intensities, we were able to show unambiguously that the bulk 3-D structure is inconsistent with $P2_1/a$ (in-phase bond alternation), and therefore the weak, sample-dependent (001) intensity results from uncorrelated local defect regions with in-phase bond alternation on adjacent chains. This observation may provide a clue for explaining the irreproducibility of extremely high conductivities claimed for the various "new, improved" forms of (CH)_x which have recently been reported.

We were able to rule out the possibility of bulk phase coexistence of $P2_1/a$ and $P2_1/n$ structures as follows. Considering the (00L) intensities alone implies the existence of 20% of $P2_1/a$ phase in our sample, while the ratio of off-axis (021) and (011) intensities place an upper limit of only 4%. The (001) intensity must therefore be associated with a local defect, for example short chain segments which correlate with neighboring longer chains in the in-phase configuration. It would be interesting to perform a comparative study of various kinds of (CH)_x to find out if a variable density of such short-chain defects can be correlated with differences in macroscopic properties, e.g. conductivity after iodine doping (see Appendix G).

E. SOLID PHASES DERIVED FROM BUCKYBALLS

1. Introduction

A new crystalline form of pure carbon was reported less than a year ago. Unlike diamond and graphite, this new material ("buckminsterfullerite") is constructed from soccer ball-shaped 60-atom molecules ("buckyballs") which are atomic-scale analogs of Fuller's geodesic domes. Chemists are claiming that these highly stable yet modifiable molecules will generate an entirely new class of organic compounds. The implications for materials science may also be far-reaching. Speculations have been made concerning applications as lubricants, selective tuneable catalysts and electrochemical energy storage materials. Additional excitement has been generated by the recent discoveries of metallic and superconducting behavior in alkali metal-doped fullerenes.

The availability of a broad range of expertise and central facilities under one roof made it possible for LRSM faculty and staff to quickly make a major impact on this rapidly growing field. Our interest was initially stimulated by a visit from Prof. R. Smalley (one of the co-discoverers of C₆₀) in October 1990, which revealed several obvious connections between his beloved buckyballs and our ongoing research: the complementarity between liquid and plastic crystals (i.e. orientational vs. positional long-range order); possible analogies between layer intercalates, doped conjugated polymers and doped C₆₀; and the prospect for rapid advancement through close coupling among synthesis, experiment, simulations and theory. We began meeting once a week to plan experiments, share ideas etc., and produced our first pure C₆₀ in late December. As of this writing 19 papers have been published or submitted by Penn faculty. The LRSM

has also established an international electronic preprint alert service, and is collaborating with Smalley to maintain his bibliographic data base. We also hosted a 2-day workshop in early August, focussing on condensed phases and superconductivity. A large number of external collaborations have already taken shape, including proposals with groups in France and Israel. The highlights of DOE-funded achievements in this exploding field are summarized below.

2. Structure, Bonding and Dynamics in Solid C_{60}

A closely-coordinated program of x-ray and neutron scattering, model calculations and molecular dynamics simulations, revealed the salient features of the solid C_{60} lattice. Pure C_{60} at 300K is a face-centered "plastic" crystal with long-range positional order ($> 1000\text{\AA}$ correlation length) but no molecular orientational order, the converse of nematic liquid crystals. It transforms to an orientationally-ordered simple cubic structure below 249K, as observed by x-ray diffraction and scanning calorimetry. Molecular dynamics simulations using a potential derived from graphite gives the correct lattice constant and reproduces the observed orientational freezing below 200K. The (isotropic) linear compressibility is the same as the c-axis compressibility of graphite, consistent with van der Waals intermolecular bonding; molecular dynamics and lattice energy calculations agree with this experiment (see Appendices H and J).

3. Alkali Metal-Doped C_{60}

Compound synthesis, x-ray scattering, molecular dynamics (Prof. M. Klein) and electron spectroscopy (Prof. W. Plummer) have been applied to study the binary alkali metal- C_{60} phases, M_xC_{60} , in order to understand the metallic and superconducting properties. Doping C_{60} to saturation with K, Rb or Cs induces a transition from fcc to a body-centered cubic compound of ideal composition M_6C_{60} . This implies a competition between elastic and electrostatic energies as the metal concentration is increased from zero, which should lead to an interesting phase diagram with some features common to layer intercalates and doped polymers (see below). Molecular dynamics simulations clearly reveal the transition from fcc to bcc with increasing metal concentration, the crossover occurring at $x = 3$ which is currently believed to be the only superconducting phase. Electron spectra are consistent with the existence of only three distinct phases ($x = 0, 3$ and 6). High-resolution photoemission shows a clear Fermi energy threshold over a large range $0.5 < x < 5$, while the Cls absorption spectra vs. x can be interpreted as linear combinations of single-phase spectra with $x = 0, 3$ and 6 . Photoemission and molecular dynamics give values for the density of states at the Fermi energy and the low-energy librational frequency respectively. Assuming that the latter is responsible for the pairing interaction, BCS theory gives a coupling constant $\lambda = 1.06$, intermediate between weak- and strong-coupling limits (see Appendix K).

4. Fluorinated Fullerenes

We have shown that C_{60} and C_{70} take up fluorine under mild conditions (300K, 100-300 torr) to yield partially-crystalline tan to yellow powdered solids. In contrast to the alkali-doped phases, the fluorinated material cannot be described as analogous to intercalation compounds. Infrared absorption shows clear evidence for C-F bonds, and mass spectrometry under a variety of source conditions shows stable species with F/C_{60} ratios ranging from 22 to 52. Weight uptake gives an average composition near $C_{60}F_{36}$, and indeed the mass distribution shows a maximum near this value. X-ray diffraction analysis gives an fcc cell with $a = 17.0\text{\AA}$, consistent with close-packed spheres of radius about $1\text{\AA}$ larger than C_{60} ("hairyballs"). Work is in progress to isolate $C_{60}F_{36}$, to achieve complete fluorination up to $C_{60}F_{60}$, and to selectively fluorinate one or two C sites using milder fluorinating agents. This work is being done in collaboration with Prof. Henry Selig (Hebrew University) who spent the summer at Penn and trained one of my students to carry out fluorine doping reactions (see Appendix L).

F. PUBLICATIONS CITING DOE SUPPORT: 1989-1991

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 No salary charged to grant:

- * Thandi Buthelezi, summer student 1990 Williams College (chemistry)
- * Dacai Xie, Penn postdoc at BNL reactor (5/89 - present)
- * Claude Mathis, visitor 6-8/90 from Strasbourg, France
- * Victoria Cajipe, visitor 6-12/90 from IPCM, Nantes, France
- * Henry Selig, visitor 7-8/91 from Hebrew University, Jerusalem
- * Oleg Zharikov, NAS visitor 3-8/90 from USSR Acad. Sci., Moscow
- * Andrey Palnichenko, NAS visitor 3-8/90 from USSR Acad. Sci., Moscow
- * Patrick Bernier, frequent visitor from CNRS, Montpellier, France

END

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