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STRUCTURE AND DYNAMICS IN LOW DIMENSIONAL GUEST-HOST SOLIDS

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PROGRESS REPORT 5-11/92
STRUCTURE AND DYNAMICS IN
LOW-DIMENSIONAL GUEST-HOST SOLIDS
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I. PROGRESS

We used both reflection- and grazing-incidence-geometry x-ray scattering to study thin films of C_{60} evaporated onto mica substrates *via* a hot-wall technique. The growth mode yields close-packed C_{60} planes which are parallel to the substrate surface and which exhibit out-of-plane correlation lengths of 850 Å. In the film plane the C_{60} is at best pseudo-epitaxial, with a 0.9° distribution of crystallite orientations, a 450 Å in-plane correlation length, and a 3.7% lattice mismatch, better than obtained by other thin film techniques but far from the accepted definition of single crystal thin film epitaxy.

It has been shown recently that sodium intercalation into C_{60} yields Na_xC_{60} ($2 \leq x \leq 6$), the most unusual feature being that Na_6C_{60} retains the face-centered cubic (fcc) structure of undoped C_{60} with a lattice constant $a = 14.38$ Å, whereas the analogous $x = 6$ phases with K, Rb or Cs are body-centered cubic (bcc). By modifying the reaction conditions, we have extended the fcc domain up to $x \simeq 10$, with a

maximum $a = 14.59 \text{ \AA}$. Rietveld refinement of x-ray data yields a structure with ideal crystallographic composition $\text{Na}_{11}\text{C}_{60}$ in which the octahedral site contains a 9-atom body-centered cluster while the tetrahedral sites are singly occupied. ^{23}Na NMR gives a three-line spectrum consistent with the proposed structure. Unlike Na_3C_{60} , the fcc structure is stable against a low-T distortion yet no evidence is found for superconductivity above 2 K.

Metallic and superconducting donor-type intercalation compounds of C_{60} are now well-established. These involve electron transfer from a sublattice of alkali metal dopants to a sublattice of fullerene molecules. Three stoichiometric phases have been identified, and a binary phase diagram describing composition regions of two-phase coexistence has been proposed. On the other hand, oxidative intercalation by electron acceptors has not been reported to date. In a recent note, Ohno *et al.* presented photoemission evidence that only minor amounts of iodine are taken up by solid C_{60} , resulting in a non-metallic product which is not a definite compound. Using different reaction conditions, we readily obtained a highly crystalline phase of ideal stoichiometry C_{60}I_4 whose alternating guest-host layer structure closely resembles that of classic intercalation compounds. The 300 K resistivity exceeds $10^9 \Omega\text{-cm}$ and superconductivity is not observed above 4 K, despite the fact that the inter-fullerene separation lies in the range of the superconducting M_3C_{60} phases ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$). C_{60}I_4 is apparently the first example of a fullerite intercalation compound with no electron transfer between C_{60} and the intercalate.

We used x-ray diffraction and diamond anvil techniques to measure the isothermal compressibility of K_3C_{60} and Rb_3C_{60} , the superconducting binary alkali metal intercalation compounds of solid buckminsterfullerene. Combining these results with the pressure dependence of the superconducting onset temperature T_c , we established a universal first-order relationship between T_c and lattice parameter a over a broad

range, $13.9 \text{ \AA} < a < 14.5 \text{ \AA}$. We also observe a small second-order intercalate-specific effect which allows us to rule out the participation of intercalate-fullerene optic modes in the pairing interaction.

Inelastic neutron scattering studies of the inter- and intrachain dynamics of polyacetylene, polyaniline and poly-paraphenylene-vinylene reveal important differences in the dominant thermal excitations. In $(CH)_x$ we find an interchain shear mode involving relative displacements of the two inequivalent chains per cell, whereas in the ring-containing materials PANI and PPV, excitations of ring dynamics dominate the low-energy spectrum. These may be interpreted in terms of the peculiar topological defects and charge states which control the current transport in these important prototype conducting polymers.

II. STUDENTS

Otto Zhou defended his thesis in August 1992 and is now a postdoc at Bell Labs, Murray Hill NJ. Qing Zhu will finish in June or September 1993. A new first-year MSE student, Mr. Arnold Stux, has joined the project as of 9/1/92; under normal circumstances he will graduate in 1997.

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IV. PROPOSED WORK

We will continue our program of synthesis, structure modeling and property measurements in fullerene intercalation compounds. A primary goal will be to find out if compounds which do not follow the "universal" correlation between lattice constant and T_c all suffer the same low-T structural distortion. Another initiative, suggested by our work on Na_xC_{60} , will be an attempt to prepare superconducting phases at some value of x in the solid solution range $3 < x < 11$ which simultaneously satisfy the requirements of a low-T stable fcc lattice and the appropriate band filling from partial ionization of the octahedral Na clusters.

Inelastic neutron scattering studies on conducting polymers will continue at NIST as soon as their new time-of-flight instrument is commissioned. This part of our program has been stymied in part by the long shutdown of the Grenoble reactor at ILL, and the severe oversubscription of the triple-axis spectrometer at Saclay. We sorely feel the need for more and better neutron instrumentation in the US.

V. OTHER SUPPORT

DOE DEFG02-87ER45254 "Structure and Dynamics in Low-Dimensional Guest-Host Systems"; \$140K awarded for FY92 (6/91 - 5/92) (this grant).

DOE DEFG05-90ER75596 "X-ray Diffractometer for Polymer Research"; \$132,645 (9/90 - 9/92, no-cost extension to 3/93 requested).

NSF-DMR91-20668 (LRSM) "Solid State Chemistry of Fullerene-Based Materials"; \$81K (7/92 - 6/93).

NATO 87/0866 "Staging in Doped Polymers: Local and Long-Range Structural Probes"; with Patrick Bernier, \$5K/yr travel (1/91 - 1/93)

NSF INT89-14555 "Collaboration on Conjugated Polymers"; \$14,160 (1/90 - 6/93) - similar amount awarded to Patrick Bernier by CNRS.

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