Vibrational and Electronic Properties
of Clusters and Ultrathin Films

Progress Report

Jeffrey S. Lannin
Penn State University
Department of Physics
University Park, PA 16802

Prepared for
The U.S. Department of Energy
Grant No. DOE DE-FG02-84ER45095

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Progress Report on Prior DOE Research for 1990-1992

Indicated in this progress report are accomplishments under DOE support of studies of vibrational and electronic states of clusters and thin films. This covers a period of approximately 26 months of research. In addition to clusters and thin films, studies of bulk fullerene and amorphous carbon are also noted. Recent activity has been primarily focused on fullerene-based materials, given recent developments, opportunities and special experimental capabilities we have developed. These are discussed in more detail in future proposed research in a separate section. During the last year we have also received a DOE Research Equipment award for a high resolution electron energy loss (HREELS) system for cluster and ultrathin film studies.

Fullerene Research

Structure of C₆₀

A large quantity (0.6gms) of pure C₆₀ was purified in a Penn State collaboration with the chemistry group of Prof. G. Geoffroy using chromatography on a substantial C₆₀ + C₇₀ mixtures obtained from Prof. R. Smalley. Diffraction measurements on the Argonne National Laboratories SEPD Instrument at the Intense Pulsed Neutron Source yielded an excellent S(Q) at 300K extending to 45Å⁻¹. Fourier transformation yielded a radial distribution function (rdf) analysis in which 13 distinct features were observed for r < 7Å. This confirmed directly the structure of C₆₀ and allowed improved values for the single and double bond distances. Significant differences with most theories (at the time) and with distances obtained for ligand molecules bound to C₆₀ were obtained. Measurements at 10K indicated the absence of rotations and longer range, interfullerene correlations extending to 30Å. A collaboration with Prof. T. Egami of the University of Pennsylvania on modeling the rdf yielded information on structural disorder in the SC phase. The results suggest that sample preparation influence orientation disorder between the two predominant interball configurations.

Dynamics of C₆₀

The bulk C₆₀ sample was employed in a collaborative, ongoing study of carbon phase inelastic neutron scattering with NIST and Ohio University (W. Kamitakahara; R. Cappelletti). These first reported density of states measurements provided information on the full range of vibrations, particularly those without infrared or Raman activity. Comparisons with theories indicated best agreement with the studies of Ho et al, though significant differences were also noted. Inelastic neutron measurements on graphite and nanocrystalline glassy carbon indicated that the major bands in the density of states are similar to those found in C₆₀. This is attributed to the primary role of three fold coordination in both systems and related bonding character. However, an ~8% softening of these bands in C₆₀ is attributable to changes in bonding character in the modified topology of C₆₀.

Raman Scattering of Fullerene-Based Systems

The extensive ultrahigh vacuum system developed in our previous cluster program was utilized for ultrathin film studies of alkali-metal C₆₀ alloys of A_xC₆₀. In situ interference enhanced Raman scattering (IERS) and photoemission (XPS and UPS) were employed to study changes in the vibrationally active and disorder induced intramolecular modes. The primary emphasis has been on evidence for electron-phonon coupling changes of special relevance for a mechanism for superconductivity at relatively elevated temperatures. Ultrathin film Raman scattering has provided a valuable, unique means of studying such changes in intramolecular modes with alkali-metal doping level, as such films form solid solutions if sufficiently thin. Detection of the range of thicknesses and the presence of different phases by Raman scattering provides a particularly valuable means of sample analysis.

The major result of the Raman studies has been to demonstrate that both low frequency, radial and high frequency, tangential modes of H_g symmetry have substantial electron-phonon coupling. This differentiates those theories that are appropriate and also point out that in detail

no current theory is correct (as of Aug. 1992) in indicating the correct modes. Specifically the importance of the $H_g(2)$ mode has not been found in current theories. While initial work focused on Rb_xC_{60} solid solutions, expansion to the other alkali-metals, excluding Li, have provided a means of determining which $H_g(i)$ modes appear to not be significant, as well as yield quantitative estimates of the magnitude of the electron-phonon coupling for the individual modes. This continues to be a quite important area, as structural disorder effects may also influence Raman line shapes.

Studies of thicker A_3C_{60} films of 400Å thickness in UHV using multichannel Raman scattering have provided additional information, that confirm the importance of $H_g(2)$ and $H_g(8)$ modes, as well as clarify the role of structural disorder in ultrathin films. In all of the Raman studies, XPS measurements have provided an independent means of determining the alkali-metal concentration, while UPS has yielded information on changes in population of LUMO bands. Recent studies of lower x solid solution materials have demonstrated a correlation between a new Raman band and additional structure in the valence states that are attributed to structural disorder.

Studies of C_{60} on noble metal surfaces have combined in situ, UHV Raman scattering and UPS to study charge transfer to C_{60} . These Raman measurements of $A_g(2)$ mode shifts employed rough surfaces in a SERS configuration (surface enhanced Raman scattering). This valuable Raman and UPS combination has allowed, through observation of a LUMO band for Ag and Cu, a demonstration of a metallic interfacial state. In contrast, Raman shifts observed for Au or several nonmetallic surfaces and the absence of a UPS LUMO band suggest possible covalent coupling and weak charge transfer. The trends observed in the SERS shifts and UPS are in accord with the high electron affinity of C_{60} and increased charge transfer as the work function of the substrate metal decreases.

Studies of atomic H adsorbed on C_{60} clusters either in the gas phase or on surfaces demonstrated large changes in the UPS spectra of C_{60} . Raman scattering (IERS) indicated that this was due to heterogeneous disorder, and not a modification of the basic C_{60} structure.

Bi clusters

Raman scattering and transmission electron microscopy have been employed to study clusters of Bi formed on disordered carbon surfaces by sputter deposition at 110K. In situ UHV studies using IERS have demonstrated a transition from a nanocrystalline, rhombohedral, semimetallic Bi cluster phase to amorphous clusters. In contrast to amorphous Bi thin films prepared at very low temperatures and which are found to be superconducting, the present clusters (island films) yield a phonon spectrum that suggests semiconducting character. With decreasing cluster size the changes in the Raman spectra suggest increasing localization of charge and formation of stronger cluster covalent bonds.

Overcoating of the Bi clusters with Ge has provided a means of removing samples from UHV for TEM measurements. XPS have been valuable in confirming that the microstructure is not significantly modified with increasing temperature or in overcoating. The TEM measurements yield size distributions, allowing a determination of the average size and estimated number of atoms for the transformation from an ordered nanocrystalline to disorder amorphous cluster phase. Approximately 1300 atom clusters are the transition size. These results provide the first specific value for a transition from a nanocrystalline structure to a modified cluster structure. (Although previous TEM studies of Au clusters have exhibited noncrystalline structures, a determination of a transition size has not been obtained)

The interaction of atomic H with Bi clusters was found to substantially modified the nanocrystalline to amorphous cluster structural transition. This was quite surprising given the temperature of ~110K. TEM studies demonstrated that H results in increased mobility of larger clusters over small to moderate distances that result in enhancing coalescence of dense cluster arrays. These results contrasted H assisted coalescence with that found to occur in its absence due to direct growth and aggregation processes.

Amorphous Carbon Structure

While appreciable interest has existed in the structure and properties of amorphous carbon (a-C) a careful rdf of well characterized material had not existed. A large sample of high purity (<3at.%H) prepared by rf sputtering was studied on the SEPD Instrument at Argonne National Laboratories, Intense Pulsed Neutron Source. The rdf demonstrated the absence of a distinct interhexagon peak at twice the first neighbor distance. This indicated that the probability for highly ordered hexagonal units was small. This implies that nanocrystalline type models for the structure of a-C are not correct and that random network models (Tersoff, Galli et al and Beeman et al) are more appropriate. At present, the latter models do not, however, yield more than moderate agreement with the rdf peak positions and widths. The Tersoff model, while best, does not exhibit the structural disorder observed. This rdf work continues to stimulate further theoretical modeling of the structure and properties of a-C.

Publications Under DOE Grant Support for 1990-1992

1. F. Li and J. S. Lannin, "Radial Distribution Function of Amorphous Carbon," Phys. Rev. Lett. 65, 1905 (1990).
2. F. Li and J. S. Lannin, "Structure of Amorphous Carbon," Proc. 20th Intern. Conf. Phys. Semicond., ed. E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 2163.
3. J. S. Lannin, "Raman Scattering and Thin Film Phenomena," Proc. NATO Conf. Kinetics of Ordering and Growth at Surfaces," 1990, ed. M. Lagally (Plenum, NY), p. 501.
4. M. G. Mitch, S. J. Chase, R. Q. Yu, J. Fortner and J. S. Lannin, "Raman Scattering and Photoemission from Bi Clusters," Proc. MRS Symposium Clusters and Cluster-Assembled Materials, ed. R. S. Averback, J. Bernolc and D. L. Nelson, MRS, Pittsburgh, PA 1991, Vol. 206, p. 49.
5. M. G. Mitch, S. J. Chase, J. Fortner, R. Q. Yu and J. S. Lannin, "Phase Transition in Ultrathin Bi Films," Phys. Rev. Lett. 67, 875 (1991).

6. R. L. Cappelletti, J. R. D. Copley, W. A. Kamitakahara, F. Li, J. S. Lannin and D. Ramage, "Neutron Measurements of Intramolecular Vibrational Modes in C_{60} ," *Phys. Rev. Lett.* **66**, 3261 (1991).
7. F. Li, D. Ramage, J. S. Lannin, J. Conceicao, "Radial Distribution Function of C_{60} : Structure of Fullerene," *Phys. Rev. Rap. Comm.* **B44**, 13167 (1991).
8. M. G. Mitch, S. J. Chase and J. S. Lannin, "Raman Scattering and Electron-Phonon Coupling in Rb_xC_{60} ," *Phys. Rev. Lett.* **68**, 883 (1992).
9. J. Lannin, "Finite Size Effects and the Dynamics of Amorphous and Nanocrystalline Materials," *J. Non-Cryst. Solids* **141**, 233 (1992).
10. R. Hu, T. Egami, F. Li and J. S. Lannin, "Local Intermolecular Correlations in C_{60} ," *Phys. Rev. B Rapid Comm.* **45**, 9517 (1992).
11. W. A. Kamitakahara, J. S. Lannin, R. L. Cappelletti, J. R. d. Copley and F. Li, "Vibrational Spectroscopy of C_{60} and Graphite Carbons," *Proc. Inter. Conf. Neutron Scatt., Oxford 1991*, *Physica B* **180-181**, 709 (1992).
12. S. J. Chase, W. S. Bacsa, M. G. Mitch and J. S. Lannin, "Surface Enhanced Raman Scattering and Photoemission of C_{60} on Noble Metal Surfaces," *Phys. Rev. B* (Sept. 15, 1992 issue), in press.
13. M. G. Mitch and J. S. Lannin, "Raman Scattering of Bi Clusters," *Phase Transitions and Coalescence Phenomena*, *Proc. Int. Symp. Phys. and Chem. Finite Systems, NATO ASI Workshop*, (Kluwer, Amsterdam, 1992) p. 477.
14. S. J. Chase, R. Q. Yu, M. G. Mitch and J. S. Lannin, "Photoemission Spectra of C_{60} Clusters with Adsorbed Metals and Nonmetals," *Proc. Int. Symp. Phys. and Chem. Finite Systems, NATO ASI Workshop*, (Kluwer, Amsterdam, 1992) p. 1317.
15. F. Li, D. Ramage and J. S. Lannin, "Confirmation of the Structure of Fullerene," *ibid*, p. 1341.
16. M. G. Mitch, S. J. Chase and J. S. Lannin, "Variations of Electron-Phonon Coupling in Alkali-Metal- C_{60} Solid Solutions," *Phys. Rev. B Rapid Commun.* **46**, 3996 (1992).

17. J. S. Lannin, M. G. Mitch, W. Bacsa and S. J. Chase, "Raman Scattering and Superconductivity of Alkali-Fullerene Materials," Proc. Spring 1992 MRS Meeting on Novel Forms of Carbon (MRS, Pittsburgh), in press.
18. M. G. Mitch, S. J. Chase and J. S. Lannin, "Raman Scattering and Superconductivity of A_xC_{60} ," Proc. NATO Conf. Clusters and Fullerenes, Trieste 1992, ed. T. P. Martin and E. Tossatti (World Scientific), in press.

Personnel

Michael G. Mitch is currently supported full time on DOE research. His Ph. D. is expected in 1993/4. Sabrina J. Chase, who has received partial DOE support (~1/3), has a 1994 anticipated graduation. Dr. Wolfgang Bacsa, a postdoctoral student, is returning to a position at the University of Lausanne in September 1992 and will be replaced by an individual who will work on the DOE Instrumentation Grant for HREELS and C_{60} cluster studies with other spectroscopic methods.

END

DATE
FILMED

5 / 20 / 93