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LDRD Final Report on Gas Separation by Fullerene Membranes

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LDRD Final Report on Gas Separation by Fullerene Membranes

Introduction

This LDRD (Laboratory Directed Research and Development) project was funded for two years beginning in October 1992 (FY93) and was designed as a multidisciplinary approach to determining the structural and physical properties of C_{60} intercalated with various gases. The purpose of the study was to evaluate the relative permeation and diffusion of various gases with an ultimate goal of finding an effective filter for gas separations. A variety of probes including NMR, X-ray and neutron diffraction; IR spectroscopy, thermogravimetric analysis and mass spectroscopy were employed on C_{60} impregnated with a number of gases including O_2 , N_2 , Ar, Ne, H_2 , NO and CH_4 . In order to increase the absorption and decrease the effective time constraints for bulk samples, these gases were intercalated into the C_{60} using pressures to several kbar. The results of these measurements which were quite encouraging for separation of O_2 and N_2 and for H_2 from N_2 led to 17 manuscripts which have been published in peer reviewed journals. The abstracts of these manuscripts are shown below along with a complete citation to the full text.

Abstracts of Published Manuscripts

"Intercalation of Molecular Species into the Interstitial Sites of Fullerene"

R. A. Assink, J. E. Schirber, D. A. Loy, B. Morosin and G. A. Carlson

J. Materials Research Z, 2136 (1992)

Molecular species were found to diffuse readily into the octahedral interstitial sites of the fcc lattice of C_{60} . The ^{13}C NMR spectrum of C_{60} under magic angle spinning (MAS) conditions consisted of a primary resonance at 143.7 ppm and a minor peak shifted 0.7 ppm downfield. The downfield shift obeys Curie's law and is attributed to the Fermi-contact interaction between paramagnetic oxygen molecules and all 60 carbon atoms of rapidly rotating adjacent C_{60} molecules. Exposure of C_{60} to 1 kbar oxygen for 1.75 h at room temperature resulted in a spectrum of seven evenly spaced resonances corresponding to the filling of 0 to 6 of the adjacent octahedral interstitial sites with oxygen molecules. The distribution of site occupancies about a C_{60} molecule provided evidence that the intercalation process is controlled by diffusion kinetics. Exposure to 0.14 kbar hydrogen gas at room temperature for 16 h filled a substantial fraction of the interstitial sites of C_{60} and C_{70} with hydrogen molecules.

"An NMR Study of the Occupation of C_{60} FCC Interstitial Sites
by Molecular Species"

R. A. Assink, D. A. Loy, J. E. Schirber, B. Morosin
Materials Research Society Proceedings, 270, 255 (1992)

The ^{13}C NMR of FCC C_{60} under magic angle spinning (MAS) conditions yields linewidths on the order of 1 Hz at fields of 4.7 T. The spectrum consists of a primary resonance at 143.7 ppm and a minor peak shifted 0.7 ppm downfield. The intensity of the minor resonance relative to the primary resonance was found to vary from 0.6 to 5.5 % depending on the sample history. The downfield shift obeys Curie's law and is attributed to the Fermi contact coupling interaction between paramagnetic oxygen molecules and all 60 carbon atoms of rapidly rotating adjacent C_{60} molecules. Exposure of the sample to 1 kbar oxygen for 1 3/4 hours resulted in a spectrum of 7 evenly spaced resonances corresponding to 0 to 6 of the adjacent octahedral interstitial sites being filled with oxygen molecules. At ambient pressure, the oxygen diffused out of the lattice on time scales ranging from hours to days.

"Buckminster Fullerenes as Lattice Sieves"

J. E. Schirber, R. A. Assink, G. A. Samara, B. Morosin, and D. Loy
Comments on Condensed Matter Physics, 16, 213 (1993)

Our studies of the interaction of various gases with C_{60} lead us to suggest that the use of fullerenes as lattice sieves for large scale separation of technologically important gases may be feasible.

"Intercalation of Simple Gases into the C_{60} Lattice"

R. A. Assink, J. E. Schirber, D. A. Loy and B. Morosin
Fullerene '93

We report the results of nmr and weight loss measurements of high pressure (to 1 kbar) loaded C_{60} . Results involving O_2 , N_2 and H_2 are discussed.

"Negative Pressure Effects in High-Pressure Oxygen-Intercalated C_{60} "

J. E. Schirber, R. A. Assink, G. A. Samara, B. Morosin and D. Loy
Physical Review B51, 15552 (1995)

We have observed unexpected and as yet unexplained negative pressure effects in high-oxygen-pressure-treated C_{60} in which the orientational ordering temperature is greatly depressed. Such effects are not observed in identical studies with nitrogen.

"The Effect of O₂ Intercalation on the Rotational Dynamics and the Ordering Transition of C₆₀"

S. A. Myers, R. A. Assink, J. E. Schirber and D. A. Loy
Proc Materials Res Soc., December 1994

We have used ¹³C magic-angle spinning (MAS) nuclear magnetic resonance (NMR) to characterize the structure and rotational dynamics of C₆₀ containing oxygen molecules located in the interstitial sites of the fcc lattice. Under normal conditions, a narrow peak at 143.7 ppm is observed for C₆₀. When exposed to oxygen at moderate pressures, several additional resonances appear in the ¹³C MAS NMR spectrum. These secondary resonances are shifted downfield from the main peak at 143.7 ppm and are due to the Fermi-contact interaction of the paramagnetic oxygen molecules with the ¹³C nuclear spins. The presence of oxygen depresses the orientational ordering transition by ca. 20 K as observed by DSC. The spin-lattice relaxation time (T₁) of each secondary peak shows a minimum near the ordering transition, indicating that this transition is not dependent on the number of oxygen molecules surrounding an individual C₆₀ molecule. The T₁ due to paramagnetic relaxation, normalized by the number of surrounding oxygen molecules, is constant. This observation demonstrates that within a give sample, the dynamics of C₆₀ molecules are independent of the number of surrounding oxygen molecules.

"Room Temperature Compressibility of C₆₀: Intercalation Effects with He, Ne and Ar"

J. E. Schirber, G. H. Kwei, J. D. Jorgensen, R. L. Hitterman and B. Morosin
Phys Rev B 51, 12014 (1995)

We report measurements to 6 kbar of the room-temperature compressibilities of C₆₀ for both the fcc and sc phases using He, Ne, and Ar as pressure media. The effects of rare-gas intercalation on the fcc-to-sc transition and on the compressibilities are discussed and we compare our results with the widely disparate literature values reported for the fcc compressibility.

"Ne Intercalated C₆₀: Pressure Dependence of Ne Site Occupancies"

B. Morosin, J. D. Jorgensen, Simine Short, G. H. Kwei and J. E. Schirber
Phys Rev 53, XXX (1996)

We report the Rietveld refinement of the structures of inert gas (Ne)-intercalated C₆₀ using time-of-flight neutron powder diffraction data. Various pressures to ~2.5 kbar at room temperature were employed. We find that only the octahedral interstices are occupied by the Ne intercalate. The pressure dependence of the Ne occupancies in the octahedral site has been determined. The cubic lattice parameter increases linearly with the amount of intercalated Ne.

"Rare-Gas Intercalation into Fullerene Interstices"

G. H. Kwei, J. D. Jorgensen, J. E. Schirber and B. Morosin

Proc. IV International Conf. on Adv. Matl. International Union of Materials
Research Society, Cancun Mexico 1995

We review our neutron diffraction studies of the intercalation of the rare gases into the interstices of C_{60} at pressures ranging from 0 to 6 kbar, primarily at room temperature, but also at other temperatures. Room temperature compressibilities of C_{60} for both the face-centered-cubic and simple-cubic phases using Ar, which does not intercalate, as the pressure medium are in excellent agreement with the earlier work of David et al., while the values for He and Ne are slightly smaller than those using Ar. The rates of intercalation and release of Ne, at a number of different temperatures, have been measured and show that, as a given temperature, intercalation is much slower than release. Structural refinements of the Ne intercalated C_{60} have been carried out for room temperature samples at many different pressures. These data suggest that Ne only intercalates into the octahedral hole and that the occupancy increases smoothly with pressure.

"On the 'Orthorhombic Form of C_{60} ': Molecular crystals Containing CS_2 "

B. Morosin, P. P. Newcomer, R. J. Baughman, E. L. Venturini, D. Loy
and J. E. Schirber

Physica C 184, 21 (1991)

Crystals of orthorhombic symmetry obtained on evaporation of CS_2 solutions of C_{60} contain solvent molecules rather than representing a new lower density form of pure C_{60} . Introduction of I_2 into the CS_2 solutions yields crystals containing solid solutions, i.e. $C_{60} 1.5(CS_2, I_2)$. Both types of crystals degrade rapidly in X-ray radiation.

"Pressure Dependence of the Orientational Ordering in Solid C_{60} "

G. A. Samara, J. E. Schirber, B. Morosin, L. V. Hansen, D. Loy and A. P. Sylwester
Phys. Rev. Letters 61, 3136 (1991)

Pressure studies of the molecular orientational ordering in solid C_{60} have exhibited three principal effects: (1) The simple-cubic (sc) to face-centered-cubic (fcc) ordering transition temperature ($T_c=249$ K) increases with pressure at a rate of 10.4 ± 0.2 K/kbar corresponding to $d\ln T_c/d\ln a_0 = -22.8$, where a_0 is the lattice parameter; (2) pressure greatly reduces orientational fluctuations of the C_{60} molecules in the ordered low-temperature sc phase; and (3) the results suggest the presence of two ordering transitions instead of one near 249 K. The implications of these results are discussed.

"Effects of Pressure and Ambient Species on the Orientational Ordering
in Solid C_{60} "

G. A. Samara, L. V. Hansen, R. A. Assink, B. Morosin, J. E. Schirber and D. Loy
Physical Rev. B 47, 4756 (1993)

The effects of hydrostatic pressure on the orientational ordering transition in solid C_{60} were investigated using helium, nitrogen, and a 50/50 (by volume) mixture of normal and isopentanes as pressure-transmitting media. The different observed responses in these media and for different samples, as well as some irreversible pressure cycling effects, have provided much insight into the ordering process. Highlights of the work include the following: (1) Lattice compression hinders the librational motion of the C_{60} molecules in the low-temperature simple cubic (sc) phase, thereby increasing T_c and stabilizing the sc phase; the effect is large; (2) the pressure dependence of T_c , along with the accurately known volume change at the transition, yield 1.7 kcal/mole and 6.5 cal/K mole for the latent heat and discontinuous change in entropy, respectively, associated with the transition; (3) T_c and its pressure dependence are influenced by the presence of ambient species in the interstitial lattice sites. Helium appears to diffuse readily into the lattice, whereas N_2 (and O_2) diffuse less rapidly and occupy octahedral sites; (4) a two-peak structure in differential thermal analysis spectra (also reported in specific-heat measurements) was observed and is believed to be due to the partial occupation of the octahedral sites by species such as N_2 or O_2 ; (5) solid C_{60} "reacts" with pentane at pressures ≥ 14 kbar and temperatures > 475 K to yield an irreversible C_{60} /pentane complex similar to that obtained by the cocrystallization of C_{60} and normal pentane at 1 kbar. These results are discussed in terms of proposed models.

"Effects of Pressure on the Orientational Ordering and Phase Transitions in
Solid C_{60} and C_{70} "

G. A. Samara, L. V. Hansen, B. Morosin and J. E. Schirber
Proceedings of AIRAPT/APS Joint Conference, p. 643 (1994)

The temperature-pressure phase diagrams of solid C_{60} and C_{70} have been determined and compared. A significant finding is the large influence of interstitial species and of the pressure transmitting medium on the orientational ordering process. The pressure results reveal different, nearly degenerate configurations in both solids, which are believed to be due to hindered molecular rotations by interstitial species, and possibly different stacking modes in C_{70} .

"Stoichiometrically Controlled Direct Solid-State Synthesis of $C_{60}H_2$ "

B. Morosin, C. Henderson and J. E. Schirber

Applied Physics A 59, 179 (1994)

The direct solid-state synthesis of $C_{60}H_2$ has been demonstrated by controlling the amount of hydrogen introduced into the reaction with C_{60} . Palladium hydride has been used as the source of hydrogen. The main product $1,2-C_{60}$ is the isomer predicted to have the lowest energy of the possible 23 isomers; in addition, small amounts of the thermodynamically most stable isomer of $C_{60}H_4$, $1,2,3,4-C_{60}H_4$, have also been obtained.

"Stoichiometrically Controlled Direct Solid State Synthesis of $C_{60}H_2$ "

B. Morosin, C. Henderson and J. E. Schirber

Mat. Res. Soc. Symp. Proc. Vol. 349 (1994)

We have demonstrated the direct solid state synthesis of $C_{60}H_2$ by controlling the amount of hydrogen introduced into the reaction with C_{60} . Palladium hydride has been used as the source of hydrogen. The main product $1,2-C_{60}H_2$ is the isomer previously predicted by computational studies to be the lowest in energy of the possible 23 isomers; in addition, small amounts of the thermodynamically most stable isomer of $C_{60}H_4$, $1,2,3,4-C_{60}H_4$, has also been obtained. To determine structural parameters by x-ray diffraction, crystal growth from various solvents yielded complex solvent-containing crystals which were examined; however, the complex nature of these crystals have so far precluded detailed crystal structure determinations.

"Effects of Pressure and Ambient Species on Orientational Ordering in Solid C_{70} "

G. A. Samara, L. V. Hansen, B. Morosin and J. E. Schirber

Submitted to Phys Rev.

The effects of hydrostatic pressure on the orientational ordering phase transitions in solid C_{70} were investigated by differential thermal analysis (DTA) using helium and nitrogen gases as pressure-transmitting media. The different observed responses in these media for the different transitions and for different samples, as well as some irreversible pressure/temperature cycling effects, have provided much insight into the ordering processes and into the influence of interstitial lattice impurities on these processes. Compression of the lattice strongly hinders the rotational motion of the C_{70} molecules, especially their high-temperature tumbling motions, and results in stabilization of the ordered low-temperature phases. This feature reflects the weak van der Waals intermolecular bonding and concomitant high compressibility of the C_{70} lattice as well as the high sensitivity of the rotational barriers to intermolecular separation. In microscopic terms, the results can be understood in terms of pressure-induced enhancement of the nesting of electron-rich and electron poor

regions of the C_{70} molecular cages. Observations of the evolution of DTA spectra during compression and as a function of time after release of pressure revealed a variety of nearly degenerate (in energy) configurations which are believed to be due to either hindered rotations of the molecules by interstitial impurities or to different stacking sequences of the monomolecular C_{70} layers. The results are compared with earlier findings on solid C_{60} .

"Role of Pressure in the Study of Fullerenes"

J. E. Schirber, G. A. Samara, B. Morosin, R. Assink, D. Loy
AIP Conf. Proc. 309, 639 (1994)

Although fullerenes and their compounds are very new and exhibit new phenomena, pressure has already been an important factor in the characterization and study of these materials. In order to illustrate this, we will review collaborative studies on: i) the effect of pressure on alkali and alkaline earth doped C_{60} superconductors, ii) the effect of pressure and pressure medium on the ordering temperature of C_{60} , and iii) the role of pressure in the study of the feasibility of using C_{60} as "lattice sieves" for separation of gases.

"Structural Properties of Vapor-Grown C_{60} Crystals"

B. Morosin, X. -D. Xiang, M. Fuhrer and A. Zettl
Appl. Phys. A57, 171-174 (1993)

Vapor grown crystals of C_{60} with thin flat triangular, rhombic or trapezoidal shapes of size to $1 \times 2 \times \sim 0.001$ mm as well as prismatic crystals typically $0.5 \times 0.4 \times 0.2$ mm have been grown using a high temperature vapor transport method. Room temperature X-ray precession photography shows these crystals exhibit diffraction patterns consistent with those for either (a) single or (b) twinned crystals of the previously reported face-centered cubic structure or (c) a more complex cell of hexagonal symmetry with $a = 10.010(2)$ Å and $c = 49.064(11)$ Å. This latter form actually is a multiple twin containing both the face-centered cubic and the close-packed hexagonal structure types. The sharp diffraction maxima for either the single or the twinned crystals demonstrate that they consist of large coherent domains and are essentially free of planar defects parallel to the twin planes.

Conclusion

The studies reported above showed that C_{60} has great potential as a gas separator. We observed (unpublished) separations of 14 for O_2 versus N_2 in a single pressure swing. This is state of the art. Unfortunately, a third year was needed to really exploit these findings. Industrial partners are being sought to extend the work.

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