

doped C_{60} (3, 6). Thin film samples (3) show a semiconductor-like upturn in $\rho(T)$ above T_c and a severely broadened transition to the superconducting state. We conclude that this behavior is not intrinsic but due to imperfections such as grain boundaries (3). In fact, our own transmission electron microscopy studies on thin C_{60} films (7) show that the grain size of freshly deposited films maintained in air at room temperature changes from $\sim 0.5 \mu\text{m}$ to $< 200 \text{ \AA}$ over a period of several days. Hence, conclusions drawn from thin film transport data may be suspect.

The quality of our resistivity data and the sharpness of the transition to the superconducting state allow a test of various fluctuation mechanisms. We have attempted to fit $\rho(T)$ near T_c to three-, two-, one-, and zero-dimensional fluctuation expressions (8). In all cases, the agreement with experimental data is poor. Hence, we conclude that K_3C_{60} displays no substantial fluctuation conductivity near the onset to the superconducting state.

The overall temperature dependence of $\rho(T)$ above T_c places constraints on normal-state transport models. Preliminary analysis indicates that the temperature dependence of the resistivity can be fit to a T^2 functional form, a result consistent with

electron-electron scattering, although electron-electron scattering has not been observed at such high temperatures in other systems. The observed temperature dependence can also be accounted for with an electron-phonon scattering mechanism (9) if there is a high-frequency contribution from the intraball phonons and a lower frequency contribution from phonons with frequencies in the range of 10 to 200 K.

REFERENCES AND NOTES

1. R. C. Haddon *et al.*, *Nature* **350**, 320 (1991).
2. K. Holczer *et al.*, *Science* **252**, 1154 (1991).
3. T. T. M. Palstra, R. C. Haddon, A. F. Hebard, J. Zaanen, *Phys. Rev. Lett.* **68**, 1054 (1992).
4. P. A. Heiney *et al.*, *Phys. Rev. Lett.* **66**, 2911 (1991).
5. L. J. Van der Pauw, *Philips Res. Repts.* **13**, 1 (1958).
6. Y. Maruyama *et al.*, *Chem. Lett.* **10**, 1849 (1991).
7. J. G. Hou *et al.*, in preparation.
8. M. Tinkham, *Introduction to Superconductivity* (Krieger, Huntington, NY, 1975), p. 253.
9. J. M. Ziman, *Electrons and Phonons* (Oxford at the Clarendon Press, Oxford, 1979).
10. This research was supported by National Science Foundation grant DMR88-18404 and by the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098. V.H.C. was supported by a National Defense Science and Engineering Graduate Fellowship.

21 February 1992; accepted 16 April 1992

Scandium Clusters in Fullerene Cages

Costantino S. Yannoni, Mark Hoinkis, Mattanjah S. de Vries,
Donald S. Bethune, Jesse R. Salem, Mark S. Crowder,
Robert D. Johnson

The production and spectroscopic characterization of fullerene-encapsulated metal-atom clusters is reported. In particular, both solution and solid-state electron paramagnetic resonance (EPR) spectra of Sc_3C_{82} have been obtained. ScC_{82} also gives an EPR spectrum, but Sc_2C_n species—the most abundant metallofullerenes in the mass spectrum—are EPR-silent even though Sc_2 is EPR-active in a rare-gas matrix at 4.2 K. The results suggest that the three scandium atoms in Sc_3C_{82} form an equilateral triangle—as was previously suggested for Sc_3 molecules isolated in a cryogenic rare-gas matrix. The spectrum of ScC_{82} has features similar to those found earlier for LaC_{82} and YC_{82} , suggesting that it can also be described as a +3 metal cation within a -3 fullerene radical anion. An implication of this work is that production of macroscopic quantities of cluster-containing fullerenes may make possible the fabrication of exotic new structures with regular arrays of metal-atom clusters isolated in fullerene molecules, resulting in a new type of host/guest nanostructured material.

The results of carbon cluster-beam experiments (1–5) and the chemical stability recently observed for LaC_{82} (6, 7), La_2C_{80} (8), YC_{82} , Y_2C_{82} (9), and FeC_{60} (10) indicate that entrapping metal atoms in

C. S. Yannoni, M. Hoinkis, M. S. de Vries, D. S. Bethune, J. R. Salem, R. D. Johnson, IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099.
M. S. Crowder, IBM Adstar, 5600 Cottle Rd., San Jose, CA 95193.

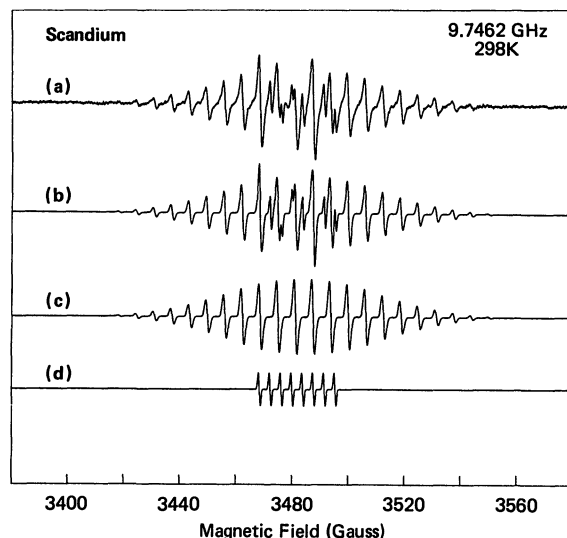
fullerene cages provides a method for isolating and stabilizing reactive species under ambient conditions. We report here the use of this method to obtain spectroscopic data on fullerene-encapsulated metal-atom clusters (11). In particular, both solution and solid-state electron paramagnetic resonance (EPR) spectra of Sc_3C_{82} have been obtained. ScC_{82} also gives an EPR spectrum, but Sc_2C_n species—the

most abundant metallofullerenes in the mass spectrum—are EPR-silent even though Sc_2 is EPR-active in a rare-gas matrix at 4.2 K (12). The results suggest that the three scandium atoms in Sc_3C_{82} form an equilateral triangle—as was previously suggested for Sc_3 molecules isolated in a cryogenic rare-gas matrix (13). The spectrum of ScC_{82} has features similar to those found earlier for LaC_{82} (7), suggesting that it can also be described as a +3 metal cation within a -3 fullerene radical anion. A broader implication of this work is that production of macroscopic quantities of cluster-containing fullerenes may make possible the fabrication of exotic new structures with regular arrays of metal-atom clusters isolated in fullerene molecules, resulting in a new type of host-guest nanostructured material (14).

Metallofullerene samples were prepared by arc-vaporization of 6-mm-diameter graphite rods that were core-drilled and packed with a mixture of scandium metal chips and graphite powder. Arc-burning was carried out in the usual manner in He at 200 torr (3, 15). The soot was collected, extracted with toluene, washed with diethyl ether, and dried. Mass spectra of the extract showed (in addition to C_{60} and C_{70}) several metallofullerenes, Sc_mC_n , with the diatomic species ($m = 2$, $80 \leq n \leq 90$) in the majority. The principal one- and three-scandium metallofullerene peaks were ScC_{82} and Sc_3C_{82} , with the C_{84} homologs present in lesser quantities. Toluene solutions of this extract were degassed with a freeze-pump-thaw cycle and sealed in quartz tubes for EPR spectroscopy.

The room-temperature EPR spectrum of such a solution is shown in Fig. 1, curve a. Qualitatively, the spectrum appears to be the superposition of two spectra centered around $g = 2$, one consisting of eight equally spaced lines of roughly equal intensity and the other a symmetrical pattern of 22 lines, with intensities decreasing monotonically outward from the spectral center. We have been able to simulate the experimental spectrum by superposing simulated EPR spectra with isotropic electron-nuclear hyperfine coupling in species that contain (i) three equivalent scandium nuclei (Fig. 1, curve c) and (ii) a single scandium nuclear spin (Fig. 1, curve d) (^{45}Sc is 100% abundant with a nuclear spin of $7/2$). The spectrum with hyperfine coupling to a single scandium nucleus consists of eight equally spaced lines with equal intensity, while the three-spin simulation generates 22 lines with relative intensities 1:3:6:10:15:21:28:36:42:46:48:48:46:42:36:28:21:15:10:6:3:1. The superposition of Fig. 1, curves c and d, yields the simulation shown in Fig. 1, curve b, in excellent agreement with experiment

Fig. 1. (a) EPR spectrum of a room-temperature toluene solution containing scandium metallofullerenes; (b) superposition of two simulated spectra arising from an unpaired electron spin coupled to (c) three equivalent scandium nuclei and (d) a single scandium nucleus.



(Fig. 1, curve a), suggesting that the EPR spectrum is attributable to just two species, which we tentatively identify as ScC_{82} and Sc_3C_{82} .

The simulation for Sc_3C_{82} (Fig. 1, curve c) has a hyperfine coupling of 6.22 G and is centered at $g = 1.9985$. This g value is close to that for LaC_{82} (7) (2.0010) and the C_{60} radical anion (16–19). The EPR spectrum of Sc_3 has been observed in an argon matrix at 4 K and could be simulated with a near isotropic g tensor (1.9933) and an axially symmetric hyperfine tensor with $A_{\parallel} = 25.52$ G and $A_{\perp} \approx 0$, corresponding to an isotropic hyperfine splitting of 8.51 G (13). The g value found in the rare-gas matrix is somewhat lower than for the Sc_3C_{82} , while the isotropic hyperfine coupling is slightly larger. On the basis of these results we propose that the three equivalent scandium atoms form an Sc_3 molecule in a doublet ground state with the geometry of an equilateral triangle—a conclusion similar to that reached for Sc_3 in a cryogenic matrix environment (also on the basis of EPR spectroscopy) (13, 20). In our case, however, this molecule is encapsulated by a fullerene. A pseudospherical C_{82} will have a skeletal diameter of ~ 8.3 Å, providing an internal cavity diameter in excess of 5 Å, which suggests that C_{82} would easily accommodate a scandium trimer (the ionic radius of Sc^{3+} is 0.732 Å) (21). We note that the magnetic equivalence of the three scandium atoms in Sc_3C_{82} provides evidence against the suggestion that the metal atoms in metallofullerenes may be incorporated in the framework of the fullerene cage (8) because random substitution of three metal atoms for carbons in the cage would not, in general, give chemical or magnetic equivalence.

The g value for ScC_{82} is 1.9998, quite close to the values for Sc_3C_{82} , LaC_{82} , and

the C_{60} radical anion. The hyperfine coupling in ScC_{82} (3.82 G) is smaller than for the Sc_3 species, but is about three times larger than the coupling measured for LaC_{82} (1.25 G) (7). We calculated the hyperfine coupling for Sc^{2+} using unrestricted Hartree-Fock wavefunctions, and obtained a value of -120 G, considerably larger than the measured value. On the basis of this difference, we propose that the scandium atom is in the $+3$ oxidation state, and that the structure is $\text{Sc}^{3+}\text{C}_{82}^{3-}$. Similar conclusions were drawn from EPR spectra of the corresponding lanthanum complex, $\text{La}^{3+}\text{C}_{82}^{3-}$ (7). However, the larger hyperfine coupling in the scandium case suggests that the electron spin may be more closely associated with the scandium atom in ScC_{82} than it is with the lanthanum atom in LaC_{82} . At low microwave power the eight-line ScC_{82} spectrum shows satellite peaks flanking each line, indicative of ^{13}C hyperfine coupling and confirming association of the scandium atom with a carbon fullerene framework.

The absence of other resonances, searched for at temperatures ranging from 4.2 K to ambient over a wide range of magnetic field strengths (0 to 0.6 T), suggests that the Sc_2C_n species (predominant relative to Sc and Sc_3 species in mass spectra) are diamagnetic. Knight and co-workers have detected an EPR spectrum for Sc_2 in rare-gas matrices at 4.2 K; our results suggest that the scandium valence electrons in Sc_2C_{82} are paired, either in metal-dimer orbitals, or in LUMOs in the fullerene cage.

In summary, we have produced fullerenes containing multiple scandium atoms and obtained evidence that suggests that the atoms form molecules within the confines of the fullerene cage. EPR spectra have been obtained for metallofullerenes

containing single and multiple (3) scandium atoms. The Sc_2C_n species detected by mass spectrometry appear to be diamagnetic. Because the metal molecules are protected from reaction by the surrounding fullerene shell, it is possible to examine them spectroscopically at ambient temperature rather than at the cryogenic temperatures required with the rare-gas matrix isolation technique. Although this technique has permitted the spectroscopic study of a vast number of metastable chemical species (22), warming such a matrix permits the guest molecules to diffuse and react. In contrast, the stability of certain fullerene-encapsulated species under ambient conditions should allow separation, purification, and crystallization—in short all of the steps which have been successfully carried out for empty fullerenes such as C_{60} .

Note added in proof: After submitting this report we learned that Shinohara *et al.* have obtained results similar to those reported here (23).

REFERENCES AND NOTES

1. J. R. Heath *et al.*, *J. Am. Chem. Soc.* **107**, 7779 (1985).
2. F. D. Weiss *et al.*, *ibid.* **110**, 4464 (1988).
3. R. E. Haufler *et al.*, *J. Phys. Chem.* **94**, 8634 (1990).
4. L. M. Roth *et al.*, *J. Am. Chem. Soc.* **113**, 6298 (1991).
5. D. M. Cox, K. C. Reichmann, A. Kaldor, *J. Chem. Phys.* **88**, 1588 (1988).
6. Y. Chai *et al.*, *J. Phys. Chem.* **95**, 7564 (1991).
7. R. D. Johnson *et al.*, *Nature* **355**, 239 (1992).
8. M. M. Alvarez *et al.*, *J. Phys. Chem.* **95**, 10561 (1991).
9. J. H. Weaver *et al.*, *Chem. Phys. Lett.* **190**, 460 (1992).
10. T. Pradeep *et al.*, *J. Am. Chem. Soc.* **114**, 2272 (1992).
11. A preliminary report of these results was presented at the Materials Research Society meeting in Boston, MA, 1 to 5 December 1991.
12. L. B. Knight, Jr., R. J. Van Zee, W. Weltner, Jr., *Chem. Phys. Lett.* **94**, 296 (1983).
13. L. B. Knight, Jr., R. W. Woodward, R. J. Van Zee, W. Weltner, Jr., *J. Chem. Phys.* **79**, 5820 (1983).
14. G. D. Stucky and J. E. MacDougall, *Science* **247**, 669 (1990).
15. W. Krätschmer *et al.*, *Nature* **347**, 354 (1990).
16. P. J. Krusic *et al.*, *J. Am. Chem. Soc.* **113**, 6274 (1991).
17. P.-M. Allemand *et al.*, *ibid.*, p. 2780.
18. A. Penicaud *et al.*, *ibid.*, p. 6698.
19. S. G. Kukolich and D. R. Huffman, *Chem. Phys. Lett.* **182**, 263 (1991).
20. W. Weltner, Jr., *Magnetic Atoms and Molecules* (Van Nostrand Reinhold, New York, 1983).
21. *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, ed. 52, 1972), p. 171.
22. *Matrix Isolation Spectroscopy*, A. J. Barnes, W. J. Orville-Thomas, A. Müller, R. Gaudfrès, Eds. (Reidel, Boston, 1981).
23. N. Shinohara *et al.*, *Nature*, in press.
24. The authors acknowledge the expedient technical assistance of R. D. Kendrick for help in activating time-averaging capability on the E-9 EPR and for assistance with the simulation program, which was kindly supplied by P. Kasai. We thank P. Bagus for the results of a Hartree-Fock calculation on Sc^{2+} used to calculate the ^{45}Sc hyperfine coupling.

11 March 1992; accepted 17 April 1992