Brinkman stressed that the two states could be stable in different regions of the phase diagram. They pointed out that because the effective interaction in ³He is coming not from lattice vibrations as in BCS theory but from the ³He atoms themselves, when the Cooper pairs form, you modify that response and therefore modify the effective interaction. So in principle you could get a stable A phase, but not in the BCS approximation.

By that time Leggett was investigating the effect of the B phase being a Balian-Werthamer state. He realized that if the dipole force was indeed present, it would affect not just the transverse resonance but also a longitudinal resonance. If the experiment were done in an unconventional type of geometry, where the rf field is polarized along the external field, you should observe a finite frequency response. In both the Anderson-Brinkman-Morel and Balian-Werthamer phases it turned out there would be a longitudinal resonance.

In the fall of 1973 Osheroff (by then working at Bell Laboratories) and Brinkman did the experiment suggested by Leggett and observed the predicted longitudinal resonance in the A phase as well as longitudinal absorption in the B phase.

Significance of superfluid ³He

Leggett feels that superfluid ³He is the most sophisticated condensed matter system for which we can claim a quantitative understanding. It's not just a

superfluid, it's an anisotropic superfluid. In an ordinary, old fashioned superconductor, he noted, "we generally believed the Cooper pairs were formed in the s state and had no interesting internal structure. The structure is more or less fixed by the thermodynamics. There's no way you can change it."

But ³He is quite different. The Cooper pairs have an internal structure, and the structure is different in the A and B phases. So, as Leggett says, "you can have all sorts of handles to tweak the system with. Because you can think of the Cooper pairs as Bose condensed, they must all behave in the same way." In ³He, both the orientation and the internal coordinates must all behave in the same way and this gives rise to spectacular effects. "If I have two helium atoms and they're about to form a Cooper pair, and they're going into the A phase, they have to decide whether they're going to have their spins oriented parallel or perpendicular to that angular momentum. The energy difference between those two configurations is really tiny, of the order of a nanodegree-way below millidegrees. So, normally we would just forget about it. However, because the pairs have to be Bose condensed, they have to decide once and for all whether their spins will be parallel or perpendicular to the orbital angular momentum. So the energy in question is now multiplied by a factor of 10²³. That was really fascinating. You have this tiny little thing, which is then amplified so spectacularly."

Vitae of the winners

David Lee earned an AB from Harvard University in 1952, served in the US Army, then earned an MS at the University of Connecticut in 1955 and a PhD in physics at Yale University in 1959. He then went to Cornell, where he has remained. He became a full professor in the physics department there in 1968.

Douglas Osheroff earned a BS at Caltech in 1967, an MS at Cornell in 1969 and a PhD in physics there in 1973. In 1972, he went to Bell Labs, where he became head of solid state and low temperature physics in 1982. In 1987, he became a professor of physics at Stanford University and served as department chair from 1993 until this year. He is currently the J. G. Jackson and C. J. Wood Professor of Physics.

Robert Richardson earned an MS at Virginia Polytechnic Institute in 1960 and a PhD in physics at Duke University in 1966. In 1967, he became an assistant professor of physics at Cornell, where he was promoted to professor in 1975. He is currently the Floyd R. Newman Professor of Physics and director of the Laboratory of Atomic and Solid State Physics there.

GLORIA B. LUBKIN

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Nobel Chemistry Prize Goes to Curl, Kroto and Smalley for Discovering Fullerenes

n 10 December, the 100th anniversary of Alfred Nobel's death, the king of Sweden will award the 1996 Nobel Prize in Chemistry to Robert F. Curl, Harold W. Kroto and Richard E. Smalley, "for their discovery of fullerenes." Curl and Smalley are professors of chemistry at Rice University, in Houston, where the three made the discovery in 1985. Kroto is a Royal Society research professor at the University of Sussex in Brighton, England.

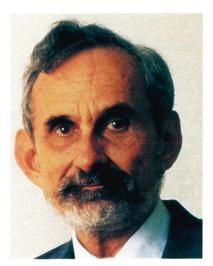
Considering the fact that diamond and graphite, the other two organized forms of pure carbon, were known in antiquity, the fullerenes are rather surprising latecomers. The paradigmatic species that started the whole fullerene business is C₆₀, the most perfectly spherical of all known molecules, with 60 carbon atoms arrayed at the vertices of a truncated icosahedron.

arbon is unique in its ability to combine with other atoms in innumerable ways. But only recently have we learned that pure carbon can form itself into a dazzling proliferation of molecular shapes.

Having seen it in September 1985 only as an astonishingly hardy peak in the mass spectrum of molecular clusters produced by laser vaporization of graphite in Smalley's supersonic cluster beam apparatus, the three chemists and Smallev's graduate students, Jim Heath and Sean O'Brien, struggled to understand why a cluster of precisely 60 carbons should be so much more robust than anything else showing up in the mass spectrum. The immediate evidence for the extraordinary stability of C₆₀ was the observation that its mass peak grew more and more prominent, relative to all the others, as the carbon vapor was subjected to longer and longer cooking times.

Soccerene

After playing around for a few days with cardboard and gum-ball models and reminiscing about geodesic structures created by the designer Buckminster Fuller, the group finally concluded¹ that the molecular structure was most likely a truncated icosahedron—a polyhedron of 20 regular hexagonal faces rounded off by 12 symmetrically spaced pentagons. When Smalley asked the chairman of the mathematics department whether he was familiar with this exotic configuration, he replied, "What you boys 've got there is a soccer ball!" Kroto, the lone European in the group, makes the



ROBERT F. CURL

excuse that when he last played soccer, many years ago, the pattern was simpler. "We considered calling this new molecule soccerene," Smalley told us. "But in the end we settled on buckminsterfullerene. It's awkwardly long, but we thought it appropriate."

The more generic name "fullerene" indicates the large class of related balllike and tubular carbon structures discovered by chemists in many countries since 1985. C₇₀ was a charter member of the family; it was the second most prominent peak in the original 1985 mass spectrum. Almost as spherical as C₆₀, it differs only by having an extra girdle of 5 hexagons around its waist. All the "buckyballs" are basically hexagonally ordered graphitelike carbon sheets distorted into closed polyhedra by intervening pentagons of carbon atoms. Euler proved in the 18th century that it takes precisely 12 interspersed pentagons to close a sheet of any number of regular hexagons into a polyhedron. "Carbon, we discovered, has a special genius for forming such structures on its own," says Smalley.

None of these geodesic configurations could be definitively confirmed in the 1980s. The microscopic quantities made by the original laser-vaporization technique were not nearly enough for chemical separation, x-ray crystallography or nuclear-magnetic-resonance spectroscopy. Molecular structure had to be deduced from mass-spectrum numerology, "shrink-wrapping" of metal atoms inside buckyballs and theoretical arguments about reactivity.

All the 60 vertices of a truncated regular icosahedron are identical; each one is the junction of two hexagons and a pentagon. Therefore such a structure should exhibit only a single NMR line. Group theory tells us that 60 is the largest number of points that can be arrayed with perfect isotropy on a

sphere. That's important for chemical stability: Each carbon atom is bonded to three others in a distorted graphitelike pattern that would prefer to be planar. The more the bonds are bent out of the plane, the more reactive a site would be. Therefore, to minimize reactivity, one would want the largest possible polyhedron, with the proviso that the bending strain is equally distributed over all the vertices. Nothing else fits the bill as well as a truncated regular icosahedron.

Suddenly in 1990 it became possible to go beyond such indirect evidence, when Wolfgang Krätchmer (Max Planck Institute for Nuclear Physics in Heidelberg) and Donald Huffman (University of Arizona) announced that they had found a way to make the fullerenes in macroscopic profusion. They had discovered that fullerene molecules were amazingly abundant in the smoke rising from a carbon arc lamp in helium, and that the C₆₀ could be extracted from the soot simply by dissolving it in benzene. Evaporating the benzene left crystals of neatly piled up C₆₀ buckyballs, the third *crystalline* form of carbon. (See PHYSICS TODAY, November 1991, page 22.) Now the configurations could be verified by x-ray crystallography and NMR spectroscopy, and the search for new fullerene forms and practical applications became a worldwide cottage industry.

The three laureates came to the buckyball business by different routes. Smalley got his chemistry PhD at Princeton in 1973, in condensed matter spectroscopy. Then he took a postdoctoral position with Donald Levy at the University of Chicago. There Smalley, Levy and Leonard Warton began to develop the technique of making cold beams of molecular clusters that was to prove crucial to the discovery of the fullerenes a decade later.



A SOCCER BALL, like a C_{60} molecule, is essentially a truncated regular icosahedron, with 20 hexagons and 12 pentagons. The carbon atoms sit at the 60 vertices, all of which are identical junctions of two hexagons and a pentagon.

"Molecular spectroscopy has always been a poor handmaiden of atomic spectroscopy," Smalley told us, "because the low-energy molecular rotational and vibrational excitations really get in the way of high resolution. So one wants to make the molecules as cold as possible." To that end, Smalley and coworkers exploited a kinematic trick: If the molecular clusters produced by laser vaporization are propelled by a puff of helium through a small nozzle into a vacuum chamber, the faster particles emerging from the nozzle bump into slower ones in front of them, thus narrowing the velocity distribution and making it possible to produce a supersonic beam whose effective temperature is only a few kelvin.

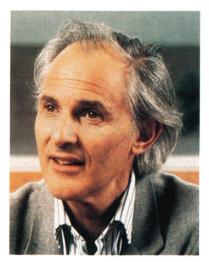
As big as a locomotive

With a very large vacuum chamber and a formidable array of downstream analytical instruments, the supersonic cluster beam apparatus that Smalley built after he moved to Rice in 1976 is as big as a locomotive. "Except for a smaller replica I helped Exxon build," Smalley told us, "there was nothing like it anywhere else. I can't imagine that we could have discovered C_{60} without it."

The apparatus was not expressly designed for the study of carbon. "We could work our way through the periodic table, studying the chemistry and physics of clusters with a few tens or hundreds of atoms," says Smalley. The work with carbon actually began in 1984 at Exxon, where Andrew Kaldor had put graphite in his apparatus and seen intriguing mass peaks at a host of even multiples of the atomic mass of carbon. But the C_{60} peak did not stand out conspicuously above the rest.

Kroto had a long-standing interest in linear carbon chains. He got his PhD at the University of Sheffield in 1964, doing spectroscopy of free radicals. After stints at the Canadian National Research Council and Bell Laboratories, he went back to England to join the Sussex faculty in 1967. "At Sussex I began thinking about the molecular dynamics of long carbon chains," Kroto told us. "It's like a cheerleader twirling a baton that can also bend and vibrate, all the while obeying the laws of quantum mechanics." Having studied such molecules by microwave spectroscopy in the laboratory with David Walton, Kroto undertook in 1975 to look for them in interstellar space by radioastronomy at the NRC. The soot pumped out in vast quantities by red-giant carbon stars, he conjectured, was coalescing into long carbon chains in the stellar atmospheres.

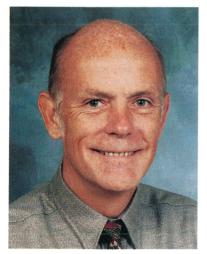
In the spring of 1984, Kroto visited Curl at Rice. When he was shown Smalley's apparatus, "what excited me most,"



HAROLD W. KROTO

Kroto recalls, "was the thought that, with graphite at the laser focus, it should be possible to simulate a carbonstar atmosphere and produce the long chains." But carbon was considered at the time to be much less interesting for useful applications than the silicon and germanium clusters Smalley and Curl were studying. So Kroto had to wait another 17 months before the machine was available for the graphite runs he wanted to do.

Curl got his PhD at Berkeley in 1957, doing infrared molecular spectroscopy. After a postdoctoral year at Harvard, learning microwave spectroscopy with E. Bright Wilson, he joined the Rice faculty. There he began by measuring microwave hyperfine structure of free radicals, moving on in the 1970s to the laser spectroscopy of molecules and transient species. In 1982 he and Smalley began their decadelong collaboration with a study of semiconductor clusters funded by the Army.



RICHARD E. SMALLEY

"When Kroto visited me in 1984," Curl recalls, "we were both keenly aware of the diffuse-interstellar-band problem": Light traversing interstellar space shows a puzzling group of about a hundred unusually broad absorption bands in the visible. Their provenence was, and remains to this day, unknown. It had been proposed that they were due to absorption by interstellar carbon chains. "So Harry and I thought we might solve this longstanding astrophysics problem by doing high-resolution carbon spectroscopy in Rick's apparatus. In the end, we never did find out whether the diffuse interstellar bands have anything to do with carbon. But in the process, we did discover the fullerenes."

Nowadays

"I got out of the fullerene business in 1992, when the big push was to find applications," Curl told us. "I just didn't feel like redefining myself as a materials scientist." Nowadays, Curl has gone back to laser spectroscopy. He is developing portable infrared lasers for monitoring atmospheric contaminants.

Kroto is also avoiding the more applied aspects of the field. Kroto, Walton and Roger Taylor head two groups at Sussex pursuing what Kroto calls "fundamental fullerene science." One group is examining the chemical reactions of fullerenes. The other is studying the growth of buckyballs and buckytubes. "It's like playing with a nanoscale erector set," says Kroto.

Smalley believes that fullerene nanotubes hold the greatest promise for useful applications: " C_{60} was the rosetta stone, but the tubes is where it's about to really flower." (See PHYSICS TODAY, June 1996, page 26.) Buckytubes are formed in much the same way as buckyballs, except that metal atoms placed in the vapor somehow deter graphene sheets from closing up into balls.

Smalley and collaborators have recently reported² the creation of what he regards as the archetypal buckytube—the cylindrical analog of C_{60} . It is a single-walled carbon cylinder just wide enough for a C_{60} buckyball to slide through. Its end caps are geodesic hemispheres of C_{240} , a very close polyhedral relative of C_{60} . "This is about the only way of wrapping a graphene sheet into a cylinder so that the electronic band structure is truly metallic," Smalley told us. "And before too long, I bet, we'll be able to grow these things in kilometer lengths."

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