

SEARCH AND DISCOVERY

Buckyballs Found to Superconduct at 52 K



The fascinating spherical molecule made of 60 carbon atoms has been the object of intensive laboratory study since 1990, when researchers reported a simple technique to manufacture such “buckyballs” in large quantities. Within a year, a crystal of C_{60} molecules had been found to superconduct^{1,2} when doped with alkali metal atoms, which cede electrons to the C_{60} lattice. By now it's known that the critical temperature can range from below 10 K to 33 K, depending on what dopant is used. But even higher critical temperatures have been expected for hole-doped buckyballs, although no one so far has succeeded in adding a dopant that will pull electrons away from the C_{60} molecules.

Enter Jan Hendrik Schön, Christian Kloc, and Bertram Batlogg at Bell Labs, Lucent Technologies. This trio has found a way to inject holes directly into the top layer of a C_{60} crystal without adding any ions to it. The hole-doped material does indeed have a higher critical temperature: $T_c = 52$ K, to be exact.³ In addition, the experimenters explored the behavior of C_{60} by varying the doping level continuously from negative to positive values. Their approach should help shed light on the still-open question of what mechanism is responsible for superconductivity in buckyballs.

The Bell Labs team used a device based on a field-effect transistor (FET). As seen in figure 1, two electrodes, a source and a drain, are laid down on top of a C_{60} crystal. The crystal and electrodes are covered with a dielectric layer of aluminum oxide, and the dielectric layer is topped with a gate electrode. A negative voltage applied to the top gate attracts holes to the top layer of the C_{60} crystal; positive voltages attract electrons. The researchers can control the sign and density of charges in this layer by changing the gate voltage. With this type of arrangement, Schön, Kloc, and Batlogg (who is now also at ETH Zurich) have made a number of remarkable discoveries (see *PHYSICS TODAY*, May 2000, page 23, and September 2000, page 17).

Peaks in T_c

The Bell Labs team found that the critical temperature had its maximum

Hole-doped carbon-60 crystals turn out to be better superconductors than their electron-doped cousins. And, if the critical temperature increases as the lattice expands, T_c might even exceed 100 K.

value of 52 K at a doping level between 3.0 and 3.5 holes per C_{60} molecule. Switching to negative charge injection, they found that T_c also peaked near 3.0 electrons per molecule but with the much lower value of 11 K. The Bell Labs results for electron doping agree with measurements on bulk samples of chemically doped C_{60} , that is, those with atoms added to the lattice. Such experiments have established that the most favorable structure for superconductivity is one with 3 electrons per molecule, or A_3C_{60} , where A is an alkali atom. With that stoichiometry, an alkali atom occupies every available interstitial site between the C_{60} molecules, which form a spherically close-packed solid having a face-centered cubic structure (see the article by Arthur F. Hebard in *PHYSICS TODAY*, November 1992, page 26). For other stoichiometries, both the lattice structure and electrical properties may be different. For example, A_4C_{60} (a body-centered tetragonal structure) is insulating.

By turning the voltage knob on their gate, that is, by “gate doping,” Schön and his collaborators explored the dependence of critical temperature on doping level, from -4.5 to $+4.5$ charges per molecule, as seen in figure 2. The hole-doped material remained superconducting, albeit

with lower values of T_c , for doping levels down to 1.7 and above 4.5 holes per molecule. For electron injection, the superconducting region was smaller, ranging from about 2.5 to 3.6 electrons per molecule. Figure 2 emphasizes the value of the gate-doping technique: To get the same curve with chemical doping, one would have to make a new sample for each point.

Chemical doping is complementary to gate doping, however, because it allows one to measure the dependence of superconductivity on lattice spacing—a significant parameter. Doping with larger atoms expands the C_{60} lattice. The wider spacing further reduces the overlap between the electronic bands of adjacent molecules and narrows the bandwidths. T_c varies inversely with the bandwidth, so that the larger the doping atom, the higher the T_c .

Batlogg told us that he and his coworkers are trying to find a way to expand the hole-doped C_{60} lattice, hoping to reach a higher T_c . In the electron-doped case, $T_c = 11$ K in a gate-doped sample, where the lattice spacing is 14.16 Å, but rises to 33 K in Rb_xCsC_{60} , whose lattice spacing is 14.56 Å. If the Bell Labs experimenters can incorporate interstitial ions that expand a hole-doped C_{60} lattice by the same amount, they anticipate a T_c well above 100 K.

Dependence on density of states?

The peak in T_c occurs at the same number of charges per molecule for both hole and electron doping. That symmetry is somewhat surprising: Naively, one might expect to find the maximum T_c at 5 holes per molecule, a level that corresponds to half filling of the valence band normally occupied by 10 electrons. In the case of electron-doped C_{60} , the peak at 3 charges per molecule does correspond to half filling of the conduction band, which can hold 6 electrons.

To gain further insight into what factors determine T_c , the Bell Labs group explored its dependence on the density of electronic states. Unfortunately, the only band calculations available are for bulk C_{60} , whereas the gate-doped samples are essentially two-dimensional, with induced charges assumed to occupy the top monolayer

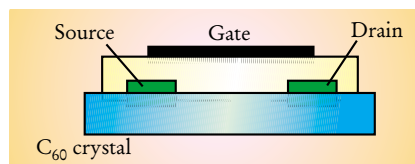


FIGURE 1. GATE-DOPING arrangement. Holes are induced in the top monolayer of the C_{60} crystal when a negative voltage is applied to the gate electrode, which is separated from the crystal by a layer of aluminum oxide dielectric (yellow). Source and drain electrodes are embedded in the dielectric to measure resistivity. (Adapted from ref. 3.)

of C_{60} . Nevertheless, comparing their data to the three-dimensional calculations, the researchers found that the peak in T_c did not coincide with a peak in the density of states. They concluded that the density of states might not be the dominant determinant of T_c .

The Bell Labs team next measured the resistivity of their C_{60} crystal above T_c because the normal-state resistivity reflects the coupling strength of electrons or holes to phonons. Arthur Hebard of the University of Florida reminded us of the old adage, “Bad metals make good superconductors.” Lead, for example, is a superconductor; gold is not. The Bell Labs experimenters compared an electron metal, made by gate doping C_{60} with electrons above T_c , to a similarly produced hole metal that had the same critical temperature. The resistivity of the hole metal was as much as six times higher than that of the electron metal, indicating that its charge–phonon coupling is much stronger. Schön, Kloc, and Batlogg conclude that the stronger coupling contributes significantly to the difference in T_c .

Dusting off old theories

Schön and his colleagues point out two factors of C_{60} that should give rise to a high critical temperature. First, the frequency spectrum of the C_{60} intramolecular vibrations extends to energies as high as 200 meV; the coupling of some of these vibrations to electronic states provides intramolecular electron–phonon coupling. Second, the density of electronic states is

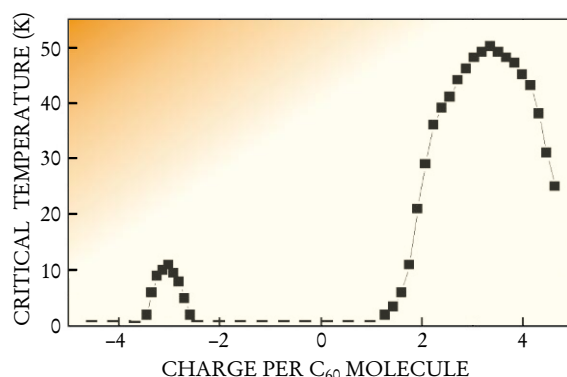


FIGURE 2. PEAKS IN THE CRITICAL TEMPERATURE T_c . Data were taken when charges were added to C_{60} crystals by gate doping. Peaks are seen when the ratio of charges to C_{60} molecules is near three for both electrons and holes. The peak for hole-doped C_{60} is higher and wider than that for electron doping. (Adapted from ref. 3.)

higher for holes than for electrons because it derives from a fivefold degenerate molecular orbital state rather than a threefold degenerate state in the case of electrons. But those are qualitative arguments. To explain the observed behavior in detail, many theorists have invoked the traditional Bardeen-Cooper-Schrieffer (BCS) theory of electron–phonon coupling. Still, as Hebard points out, some aspects of the data remain unexplained.

The results on hole-doped C_{60} are bound to revive interest in theories of electron–electron correlations as a mechanism for superconductivity. The case for electron interactions was made in 1991 by Sudip Chakravarty and Steve Kivelson of UCLA, along with Martin Gelfand (now at Colorado State University).⁴ Two aspects of the hole-doped data further strengthen

the case against a phonon mechanism, say Chakravarty and Kivelson. First, it’s hard to get a T_c as high as 52 K from phonon coupling alone without introducing instabilities. Second, it’s hard to explain by phonon mechanisms alone what the two theorists believe is a rather sharp drop-off in T_c as a function of doping. Others agree that electron–electron correlations have a large enough energy scale to yield a high T_c , but the challenge is to get the required attractive pairing out of repulsive interactions. A number of observers think that the answer may well lie in a combination of the two mechanisms.

Batlogg points out that phonons in the doped buckyballs exist in a new regime—one in which their energies are comparable to the Fermi energy. This new regime requires a new approach even to BCS models because the conventional method of calculating T_c involves expansion in the ratio of the phonon to the Fermi energy.⁵

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4. S. Chakravarty, S. A. Kivelson, M. P. Gelfand, *Science* **254**, 970 (1991).
5. See, for example, S. Chakravarty, S. Khlebnikov, S. Kivelson, *Phys. Rev. Lett.* **69**, 212 (1992).

Disappearing Atmospheric Neutrinos Don’t Seem to be Turning Sterile

For some time now, we’ve had overwhelming evidence that a significant fraction of the muon neutrinos (ν_μ) produced by decays in cosmic-ray showers in the upper atmosphere are somehow disappearing before they can get to an underground neutrino detector. Four years of data from Super-Kamiokande, the 50-kiloton water-Čerenkov detector in Japan, have made a strong case that these missing atmospheric ν_μ ’s are being transformed by “neutrino oscillation” into neutrinos of some other sort. But there was no good evidence of just what sort these other neutrinos might be. (See PHYSICS

Super-Kamiokande data strongly disfavor hypothetical sterile neutrinos as partners in the oscillation of neutrinos from cosmic-ray showers.

TODAY, August 1998, page 17.)

Now, at last, the Super-Kamiokande collaboration has published the results of its assault on this experimentally difficult question.¹ Any new evidence of neutrino oscillation and its detailed character is a subject of considerable excitement, because neutrino oscillation promises to be our first glimpse of new physics beyond the all-too-successful standard model

of particle theory.

“We find,” writes the collaboration, “that oscillation between ν_μ and tau neutrinos [ν_τ] suffices to explain all the results in hand.” The paper rejects, at the 99% confidence level, the principal competing hypothesis—namely, that ν_μ is oscillating with a putative “sterile” neutrino species that is impervious to the normal weak interaction. (The data have long since ruled out a third possibility—that the missing atmospheric neutrinos might be turning into electron neutrinos [ν_e].)

Why sterile neutrinos?

Why should anyone entertain some-