Even a small fraction of un-ionized hydrogen distributed throughout the intergalactic medium at $z \approx 6$ would have rendered the flux in the trough region undetectable. "Therefore," the Sloan team cautions, "the existence of the Gunn–Peterson trough, by itself, does not indicate that the quasar is being observed prior to the reionization epoch."[2] One has to consider how abrupt or gradual is the increase of absorption with increasing redshift. To that end, the team has looked at how the effective optical depth of the neutral hydrogen that's absorbing the quasar light depends on the redshift at which the absorption is taking place (see figure 2). An optical depth of τ means that Ly-α absorption along the line of sight has dimmed the quasar's ultraviolet emission by a factor of $e^{-\tau}$.

Figure 2 plots the optical depth for various z absorption intervals as calculated from the observed spectral intensity of the Sloan survey's four highest-redshift quasars in the corresponding wavelength intervals blueward of the Ly-α emission peak.[2] The optical depth $\tau = 5$ for the highest z interval—corresponding to the reported Gunn–Peterson trough—is a lower limit, the trough showing no discernible flux.

The curve in the figure shows the gradual increase in optical depth one would get—in the absence of a reionization phase transition—simply

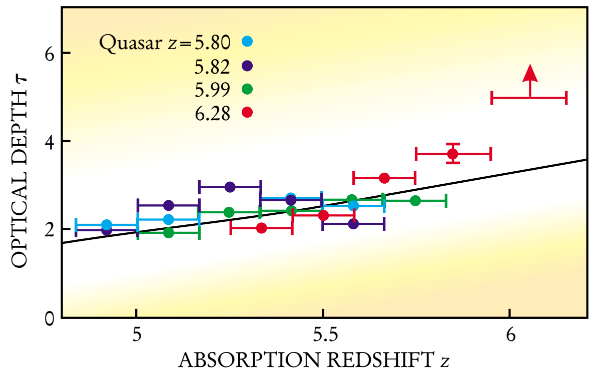


Figure 2. Optical depth due to Lyman-α absorption by neutral hydrogen grows as the redshift z at which the absorption took place increases. The data are from the spectra of the Sloan survey's highest-redshift quasars. The rightmost data point, representing a spectral trough with no discernible flux, is a lower limit. With increasing z, the data pull away from the curve that shows what one expects simply from the greater abundance of Ly-α clouds at earlier times, suggesting that the intergalactic medium also had more neutral hydrogen in that epoch. (Adapted from ref. 2.)

from the expected increase in the number density of Ly-α clouds with increasing z. Above $z = 5.8$, the measured optical depths appear to be pulling away from the curve. So, above and beyond the greater abundance of Ly-α clouds at $z \gtrsim 6$, the intergalactic medium between the clouds in that epoch had a lot more neutral hydrogen than it would have in the later epoch.

Djorgovski and company, having availed themselves of a six-hour exposure at the Keck II telescope to produce a very high signal-to-noise spectrum of the $z = 5.73$ quasar, found a revealing discontinuity that had not been evident in the earlier low-resolution spectrum: "a dramatic increase in the optical depth"[3] on the blueward side of 7550 Å. They interpret this incipient spectral trough to mean that $z = 5.2$, the Ly-α absorption redshift corresponding to 7550 Å, is perhaps the last gasp of a rather extended reionization transition.

To map out the reionization of the cosmos in greater detail, observers will need more lines of sight to quasars at the highest redshifts. The Sloan survey expects ultimately to bag a total of about 20 quasars with $z \gtrsim 6$. If the reionization transition was far from uniform, different lines of sight may tell different stories.

Bertram Schwarzschild

References

1. X. Fan et al., http://arXiv.org/abs/astro-ph/0108063, *Astron. J.* (in press).
2. R. H. Becker et al., http://arXiv.org/abs/astro-ph/0108097, *Astron. J.* (in press).
3. S. G. Djorgovski, S. Castro, D. Stern, A. Mahabal, http://arXiv.org/abs/astro-ph/0108069, *Astrophys. J. Lett.* (in press).
4. R. Barkana, A. Loeb, *Phys. Rep.* **349**, 125 (2001).

Buckyball Crystals Made to Superconduct at 117 K

By slipping molecules between C_{60} spheres in a crystal, researchers have raised the critical temperature as high as those of many copper-oxide superconductors.

The discovery in the early 1990s that C_{60} crystals could superconduct at temperatures of several tens of kelvins raised hopes that such "buckyballs" might rival the copper-oxide superconductors, whose T_c's go as high as 150 K under pressure. Those hopes have now been fulfilled.

The first C_{60} superconductors were made by incorporating alkali atoms into the spaces between the closely packed C_{60} spheres. These atoms acted as electron donors because their outer electrons were quickly stripped away by the buckyballs, which have a high affinity for electrons. Unfortunately, T_c seemed to reach a maximum of 40 K, obtained by doping C_{60} with rubidium atoms. Last year, while working at Bell Labs, Lucent Technologies, Jan Hendrik Schön (also of the University of Konstanz, Germany), Christian Kloc, and Bertram Batlogg (now at ETH Zürich) took T_c up to 52 K by finding a way to inject holes instead of electrons (see Physics Today, January 2001, page 15). Nice, but still far from the T_c region reached by the cuprates.

The achievement of 52 K was only a taste of things to come, however. The same Bell Labs–ETH team noted at the time that the T_c for electron-doped C_{60} increases with the size of the dopants: Larger dopants spread the C_{60} molecules farther apart and lead to higher values of T_c, by as much as a factor of 3 for a small percentage change in lattice spacing: When the C_{60} molecules are farther apart, the energy bands grow narrower, so that the density of states—and concomitantly the T_c—gets higher. Perhaps, the trio reasoned, the same trend would also govern hole-doped crystals.

There was certainly room to expand the C_{60} crystal. Unlike in electron doping, in which electrons are brought in by the intercalated alkali atoms, the holes are added to the crystal electronically. The T_c of 52 K had been measured on a C_{60} crystal with excess holes but no intercalated atoms. For the new study, the researchers added neutral molecules to expand the crystal, hoping to realize the promised gain in T_c.

They have now succeeded in their quest.[1] By intercalating molecules of tribromomethane ($CHBr_3$) into the C_{60} lattice, the experimenters changed the cubic lattice constant from

14.16 Å to 14.43 Å and thereby raised T_c to 117 K. As shown in the top panel of the figure, the higher the hole concentration, the higher the T_c, up to around 3–3.5 holes per C_{60} molecule. At this doping level, the critical temperature increases from 52 K to about 80 K and 117 K with insertion of trichloromethane ($CHCl_3$) and $CHBr_3$, respectively, as seen in the bottom panel of the figure.

Electronic doping

The finding of $T_c = 117$ K for hole-doped C_{60} is only the latest in a continuing series of feats that Schön, Kloc, and Batlogg have performed in the past two years. Thanks to a unique capability they have developed for adding charges to organic crystals by means of a field-effect transistor and for producing exceptionally high-quality crystals, Batlogg and his colleagues have seen both superconductivity and lasing in pentacene crystals, and have also demonstrated the quantum Hall effect there (see PHYSICS TODAY, May 2000, page 23, and September 2000, page 17). Their capability, which several groups are reportedly trying to emulate, is yielding much new physics. Zachary Fisk of Florida State University says, "Their program is fantastic. They are creating electronic states you couldn't otherwise produce."

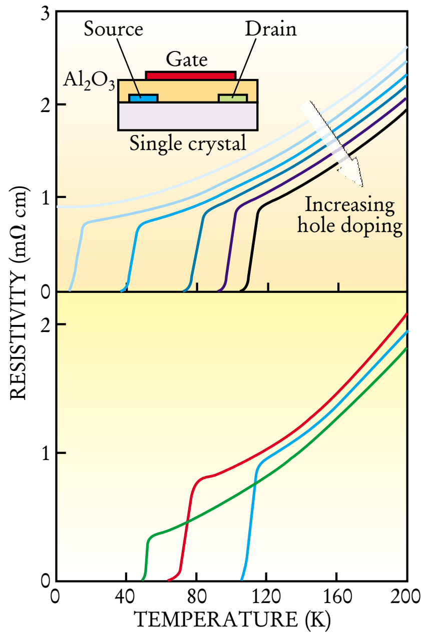
The method for injecting charges is shown in the inset in the figure. When a voltage is applied to the gate, charges of opposite sign accumulate on the interface between the insulating aluminum oxide layer and the single buckyball crystal. In this way, the experimenters can dope the crystal with either electrons or holes, depending on the sign of the gate voltage. The resistivity is measured by monitoring the current that flows from the source to the drain electrode. The experimenters must have crystals of exceptional purity; otherwise, the charge carriers can be trapped locally.

The magnitude of the gate voltage controls the degree of doping, and the doping determines the onset of superconductivity, as seen in the figure. There is considerable evidence that the charge carriers are all confined to a single layer of molecules at the surface of the crystal. So what's seen is superconductivity in two dimensions.

Picking a winner

In searching for a compound that would expand the C_{60} crystal by just the right amount, the Bell Labs–ETH team drew on numerous studies of intercalated compounds, including previous measurements[2] of the lattice parameters of C_{60} intercalated with $CHBr_3$ and $CHCl_3$. Kloc had had experience slipping those molecules from solution into a C_{60} lattice.[3] Unlike the case of alkali metal atoms, in which the transfer of electrons results in ionic bonding between the intercalated atoms and the C_{60} lattice, the $CHCl_3$ and $CHBr_3$ molecules remain neutral; with them in place, the crystal barely holds together. Still, the experimenters hope to find another molecule that will expand the lattice spacing by another percent because just that small amount can increase T_c to 150 K. If they do succeed, the results will be of interest for a limited range of applications: "You can't make wires out of this stuff," says Batlogg, "but the equivalent of thin-film electronics will be feasible."

"The implications of this work are gigantic," said Robert Cava of Princeton University. "They show us that the only thing that's stood in the way of finding more 100-K superconductors is



ONSET OF SUPERCONDUCTIVITY in C_{60} crystals varies with the degree of hole doping and with the size of the intercalated molecules. As seen in the top panel, when tribromomethane ($CHBr_3$) molecules sit between the C_{60} spheres, the critical temperature T_c (where resistivity drops) gets higher for higher levels of hole doping. As seen in the bottom panel, $T_c = 52$ K for a pure C_{60} crystal (green curve) and rises to 80 K and 117 K, respectively, when $CHCl_3$ (red) and $CHBr_3$ (blue) molecules slip into the lattice. The inset shows the field-effect transistor setup that electronically "dopes" charges into the single crystal.

thermodynamics." According to a prevailing view, he explained, the same interactions that give rise to conventional superconductivity can also break crystal structures apart or cause structural distortions that change the electronic states at the Fermi energy and thus kill the potential for superconductivity. Normally, compounds are made by heating the components together at high temperatures; that process gives the system the energy needed to overcome the activation barriers and reach its thermodynamic ground state, where distortions set in. But Batlogg and company have foiled thermodynamics by forming their compound, with the correct size and electron count, at low temperature. The same trick can be tried on other materials, Cava suggested.

Schön, Kloc, and Batlogg are now looking for superconductivity in both electron- and hole-doped C_{70}. If an electron–phonon mechanism is responsible for superconductivity in these materials, one would anticipate a lower T_c for C_{70} because of the weaker electron–phonon coupling expected in those molecules. The next step would then be to turn to smaller molecules such as C_{36}, where the coupling, and hence the T_c, is expected to be even higher than in C_{60}.

The new results on C_{60} will no doubt stimulate a renewed look at superconductivity in the fullerenes. Although an electron–phonon mechanism has been a leading candidate to explain electron pairing in these materials, the question has never been fully settled. What's the role, for example, of the very high-frequency intramolecular vibrations of the buckyballs, or of the electron–electron interactions? For superconductivity governed strictly by electron–phonon interactions, some theorists predicted in the 1970s that T_c would be limited to about 30 K. That assertion is clearly challenged by the 117-K result.

BARBARA GOSS LEVI

References

1. J. H. Schön, C. Kloc, B. Batlogg, *Science Express*, 31 August 2001. See http://www.sciencexpress.org.
2. M. Jansen, G. Waidmann, *Z. Anorg. Allg. Chem.* **621**, 14 (1995).
3. C. Kloc, P. G. Simpkins, T. Siegrist, R. A. Laudise, *J. Cryst. Growth* **182**, 416 (1997). ■

CORRECTION: August, page 14—In our story on solar neutrinos, the attributions to SNO and Super Kamiokande were inadvertently switched in figure 3 and its caption.