



RESEARCHERS FIND EXTRAORDINARILY HIGH TEMPERATURE SUPERCONDUCTIVITY IN BIO-INSPIRED NANOPOLYMER

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PAUL GRANT is in the business of tomorrow's physics at the Electric Power Research Institute in Palo Alto, California. As the lead technical forecaster at EPRI, he reconnoiters and assesses both current and anticipated developments in frontier science and technology, looking for their potential impact on the global energy enterprise.

Prior to joining EPRI in 1993, he spent 28 years at IBM's Almaden Research Center, where he investigated the fundamental science of exotic superconductors, conductors and magnetic materials. He says he wrote this essay out of frustration and revenge for the years he spent pursuing high T_c in organic metals when he should have started out with copper oxide perovskites!

He received his PhD in applied physics from Harvard University in 1965. Frequently sought out by the media for commentary on developments in superconductivity, he has been quoted in leading US and international newspapers and widely circulated weekly periodicals, and has appeared on several television specials on superconductivity.

Forty-two years ago, Johannes Georg Bednorz and Karl Alex Müller startled the world with their unexpected discovery of superconductivity in layered copper oxide perovskites at temperatures substantially higher than previously thought possible. The history of this breakthrough is well known, and a large number of related compounds were found over the succeeding years, culminating in 2002 with Au-2223—a triple-layer CuO complex with an ambient-pressure transition temperature of 175 K, synthesized by Paul Chu and his collaborators in Houston. Such materials have found a number of communications and electric power applications, especially in distribution cables, transformers and passive RF filters, but remain limited by the need for cryogenic packaging.

Now that limitation might be the stuff of history. At last month's general meeting of the North American Physical Society (NAPS), held in Cuernavaca with VR-holo simul-sessions in Waterloo, Newark, Wichita and Victoria, a collaboration between scientists at the Combined Universities of Ensenada-La Jolla (CUELJ) and the Harvard-MIT Center for Biosynthetic Engineering (HMCBE) announced the discovery of superconductivity at greater than 600 K in a laboratory-created, computationally designed polymer with structural properties akin to DNA. It is widely believed that the discovery could profoundly affect the future course of global energy development.

Organic roots

In the 1960s, physicist William Little

of Stanford University envisioned the possibility of very high temperature superconductivity in specially designed organic chain systems.¹ At that time, the prevailing Bardeen-Cooper-Schrieffer (BCS) theory successfully explained all known superconductivity as being mediated by electron-phonon coupling. Little observed that BCS could apply to any fermion pairing sustained by a general boson field, including, for example, one derived from excitons or magnons. In the weak-coupling limit, the BCS transition temperature, T_c , is typically about 10 K. Even the strong-coupling variant of BCS developed by William McMillan and Gerasim Éliashberg suggested that superconductivity mediated by lattice vibrations would not be possible above 30–40 K: To paraphrase Berndt Mathias, "You can't make a crystal structure that would be stable under such strong interactions."

Little's concept involved replacing the phonons—characterized by the Debye temperature—with excitons, whose much higher characteristic energies are on the order of 2 eV, or 23 000 K. If excitons were to become the electron-pairing "glue," superconductors with T_c s as high as 500 K might be possible, even under relatively weak coupling conditions. Little even proposed a possible realization of the idea: a structure composed of a conjugated polymer chain (polyene) dressed with highly polarizable molecules (aromatics) as side groups. Simply stated, the polyene chain would be a normal metal with a single mobile electron per C–H molecular unit; electrons on separate

units would be paired by interacting with the exciton field on the polarizable side groups.

A major problem, however, was the inherent instability of such low-dimensional metals to dimerization—the formation of a standing charge density wave—and the resulting gap in the Fermi surface that produced an insulating state. Equally serious was the detailed theoretical examination in the 1970s by Little and Hanoch Gutfreund² of the electron–exciton ($e-X$) coupling dispersion that would pair the electrons far enough away from the side groups to prevent plasma shielding of the coulombic interaction necessary for exciton formation. Both demands were deemed difficult, if not impossible, to accommodate simultaneously in an actual structure at the time.

Nonetheless, the 1970s did see a number of investigations of potentially superconducting organic systems, mostly based on charge-transfer salts. In 1980, Denis Jérôme (University of Paris, South, in Orsay) and Klaus Bechgaard (University of Copenhagen) discovered that some Lewis acid salts became superconducting around 1 K, although not by Little's mechanism. In these so-called Bechgaard salts, T_c eventually reached only 12 K by the mid-1990s and interest soon waned in the pursuit of high-temperature organic superconductivity... until now.

Spring 2027: The bud blooms

Interest renewed when scientists at the CUELJ Instituto de Investigaciones en Materiales (IIM), a center that specializes in computationally designed materials, began applying their recently developed All-Interaction Partition Function/Self Consistent Field (AIPF/SCF) algorithm to test some of Little's early ideas. A *tour de force* numerical attack such as this on cooperative phenomena in quantum solid-state chemistry was long believed not possible due to the difficulty of obtaining enough precision to accurately determine tiny differences between huge numbers—the gap energies between ground and excited states. The AIPF/SCF method circumvents this difficulty by ferretting out various quasiparticle formations, then adapting the representation basis accordingly as the iteration proceeds toward self-consistency. “Our initial findings essentially proved Gutfreund right,” said Diego Grant-López, IIM's director. “In Little's most elementary conception, the $e-X$ dispersion could not be tweaked to yield an attractive interaction. Moreover, the ‘bare’ 1D formulation produced a large charge density wave

gap at all temperatures as expected.”

The first step was thus to find a variant of the simple chain and side group model that exhibited structural stability against a charge density wave transition. “We started by looking at chiral structures similar to Linus Pauling's old alpha-helix chains,” commented Pamela Morales, lead materials designer at IIM, “except we varied the period of the helical pitch with a Fibonacci series of methyl/hydrogen cation substitutions on a cis-polyacetylene backbone.” The hope was that such a quasiperiodic structure would frustrate dimerization. It worked, but as before, $e-X$ pairing was absent.

“We also began to realize that one reason for the unusual character of Gutfreund's $e-X$ dispersion relation was the essential asymmetry of Little's original design—just one chain and one set of side groups,” said Morales. That led the group to consider double-helical structures analogous to RNA/DNA biological forms. “If materials science is an art, we decided to imitate life,” quipped Morales, “so we kept the quasiperiodic nature of the backbone, but then replicated it on the other side of the side groups, which now cross-linked the two chains.”

By late August of last year, the early returns were in. “We were all ‘mucho muy feliz,’ to put it mildly!” Grant-López told us. “We had expected the pair state to occur not only on each chain separately, but also between particles on opposite chains—and that is just what happened.” A T_c of at least 500 K was predicted, with a κ (London penetration depth divided by the Pippard coherence length) on the order of 100, making it definitely type II superconductivity.

Building with Eigler derricks

The next task was to do some “real chemistry” and actually try to synthesize the compound, which the team nicknamed “Little's Elixir,” in honor of the father of the structural concept and its biomedical analogy. In early September, the IIM workers turned to Stephanie Greene's group at Harvard-MIT, specialists in the use of Eigler derricks—a set of nanomanipulation tools based on scanning tunneling microscopy and pioneered by IBM researcher Donald Eigler around the turn of the century. IBM had hoped that Eigler derricks would lead to a new wave of nanoscale digital logic technology, but no one has yet overcome the extremely high quantum fluctuation error rates inherent in bistable devices only a few nanometers on a side. Instead, and quite unexpectedly, Eigler derricks proved to be

a revolutionary tool for biosynthesis, and they are used extensively today by pharmaceutical and genetic technology companies. As HMCBE graduate student Do-Yang Carolan put it, “Little's Elixir presented a novel synthetic challenge for us. Never before had we attempted a complex organic structure with such a customized charge distribution.”

Additionally, the HMCBE researchers had usually just built a few thousand-atom-sized templates of a given organic structure, and then self-replication would complete the assembly. The aperiodicity of the new superconductor, however, required the detailed positioning of more than 200 000 atoms in a micrometer-sized package, a task that took three shifts of nanotechnologists working around the clock 47 days to complete. BCS-like superconductivity was detected by scanning squid microscopy and nanocalorimetry. The dependence of magnetization on temperature followed the venerable Ginzburg-Landau model, even in this exotic material, which suggested that the transition temperature was somewhere around 650 K. It was only a minor nuisance that T_c could not be determined more precisely; Little's Elixir decomposes at 541 K!

In the enemy camp

After submitting their findings to the NAPS's prestigious *Biblioserver*³ technical journal, and during the Winter Solstice retreat, Grant-López and Greene boarded the Boston-Moscow shuttle with several of the first handcrafted samples of Little's Elixir. They were to visit the group of Vladimir Shegolev at the European Union Institute for Materials Science at Chernogolovna, CUELJ's chief competitor in exotic-compound research. The North Americans had e-posted a prerelease copy of their *Biblioserver* submission and found the Europeans already hard at work on their own confirmation. The North American samples were immediately tested and their superconductivity verified. By this time, Greene's students back home had begun optimizing the synthetic route, cutting atomic construction time in half. Armed with that new knowledge, the Chernogolovna workers took only two weeks to obtain synthesis confirmation as well.

Although the experimental results have received almost universal acclaim, the theoretical explanation has its skeptics. “This discovery is truly monumental, but I'm not going to be convinced that the superconductivity they observe is due to $e-X$ coupling based on mere number crunch-

ing," said McGill condensed matter many-body theorist Pierre Berlinsky-Laughlin during a recent Jackson Hole Conference on low-dimensional quantum systems. "There's a lot more work that needs to be done before the fat lady sings. Some early attempts to modify the pairing strength by optically pumping the singlet exciton band have had no effect, and one of Shegolev's structural modifications shifting the bridge-group singlet energy upward by 1 eV should have produced a sort of isotopic shift, and it didn't," Berlinsky-Laughlin continued. Even some at CUELJ are skeptical of Grant-López's interpretation. Physics department chairman Yitzak Miguel Schuller commented, "Little's model was often criticized as naive by many of his contemporaries, but interesting discoveries are sometimes made for the wrong reasons—finding new superconductors is a great historical example. I suspect we're about to learn a lot about one-dimensional quantum fluids as a result of the theoretical attention now being focused on this discovery."

Where might it go?

As for eventual applications, NAPS minister for energy Malcolm X Dynes stated in early April, "It's simply too soon to tell. We now have a mature technology in copper oxide perovskite-coated conductors that works very well in substation cable and transformer applications. There's no assurance we can scale up the new micrometer-level effect into thousands of kilometers of wire. Of course, should that be possible, it could have profound consequences. For example, the NAF tricouncil is recommending construction of two 100-gigawatt nuclear power reactor clusters over the next 20 years, one on the coast of Labrador, the other near Hermosillo. They would replace more than 120 fossil fuel plants and permit draining several large North American hydro reserves as part of our continuing program to reduce atmospheric CO₂ loading, and restore an appreciable portion of the continental wilderness. That's a massive amount of energy to move from such centralized generation points. An economic ambient-temperature superconductor could use overhead transmission towers, representing tremendous savings in refrigeration, vacuum and power corridor requirements."

Perhaps Grant-López has the most balanced view. "Look," he says, "there's something new on the planet. We're going to have a lot of fun trying to understand it, and we'll no doubt have a lot of grief along the way trying

to use it. The low dimensionality and poor flux pinning in copper oxide perovskites were a real headache, and these new organic chain compounds are likely to be even worse. Yet we made something useful out of the former. I'm reminded of a story about my father, a fan of 1960s and 1970s rock music. When things got tough he would quote some lyrics from a popular group of the time, the Rolling Stones: 'You can't always get what you want, but if you try sometimes, you just

might find you get what you need.' That's how it'll be with Little's Elixir."

References

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