SUPERCONDUCTIVITY: FROM PHYSICS TO TECHNOLOGY

It took half a century to understand Kamerlingh Onnes's discovery, and another quarter-century to make it useful. Presumably we won't have to wait that long to make practical use of the new high-temperature superconductors.

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Superconductivity was discovered in 1911 by Heike Kamerlingh Onnes in Leiden.[1] That discovery can be traced to the steady advance in laboratory techniques for obtaining ever lower temperatures that began when Louis Cailletet in France and Raoul Pictet in Switzerland succeeded in liquefying trace amounts of the "permanent gases," nitrogen, air and hydrogen. These gases were so named because previous attempts to liquefy them, by Michael Faraday among others, had been unsuccessful.[2]

Low-temperature physics emerged at about the same time as *Physical Review* itself, when Z. F. Wroblewski in Cracow succeeded in condensing experimentally useful quantities of liquid air in 1891. He found that the resistivities of pure metals had curious temperature dependences: It looked as if their resistances would vanish at nonvanishing temperatures. This intriguing possibility generated theories of the limiting low-temperature behavior that predicted everything from zero resistance to infinite resistance. Interestingly enough, today's theories still do that!

The following year James Dewar in England invented the vacuum-insulated, silver-plated glass vessel that bears his name, which enabled him to obtain experimental quantities of liquid hydrogen and proceed farther down the temperature scale. There he found that the metallic resistivities did not vanish; their temperature dependences simply flattened out.

Finally, less than two decades after William Ramsay discovered that helium exists on Earth, Kamerlingh Onnes succeeded in liquefying it. Liquid helium extended the range of temperatures available for experiment downward by another order of magnitude. Three years later Kamerlingh Onnes and his student G. Holst discovered the remarkable discontinuous disappearance of the electrical resistance of a mercury sample at a critical temperature T_c as it was cooled in liquid helium. In further experiments, a persistent current was induced that showed no measurable decay. The new phenomenon was called "supraconductivity," meaning literally "beyond conductivity." That name seems to me more appropriate than the one we use today.

The Leiden experimenters had high hopes that they were witnessing the birth of a new electromagnetic technology. They knew that the energy cost of refrigerating a superconducting electromagnet would be vastly less than the Joule heat dissipated in operating a conventional one. It was soon found, however, that normal resistance returned *below* T_c in the presence of a magnetic field above a critical limit H_c or a current above a critical limit J_c. Both of these critical parameters, alas, were low enough to thwart any hopes of prompt technological development.

In 1933 the key discovery of perfect diamagnetism by Walter Meissner and R. Ochsenfeld in Berlin showed superconductivity to be a reversible thermodynamic phenomenon. There soon followed the two-fluid model of Cornelis Gorter and Hendrik Casimir, and Fritz and Heinz London's equations describing the electrodynamics of the phenomenon in terms of surface currents that limit the magnetic field to a penetration length λ. Brian Pippard's investigation of λ as a function of the electron's mean free path led to the nonlocal extension of the London theory.

In Russia, investigations of the intermediate state in which superconducting regions coexist with normal regions over a range of external magnetic fields led in 1950 to the Ginzburg–Landau theory,[3] which generalized Lev Landau's theory of phase transitions to include a spatially dependent, complex order parameter. The remarkable intuition underlying this new theory became evident

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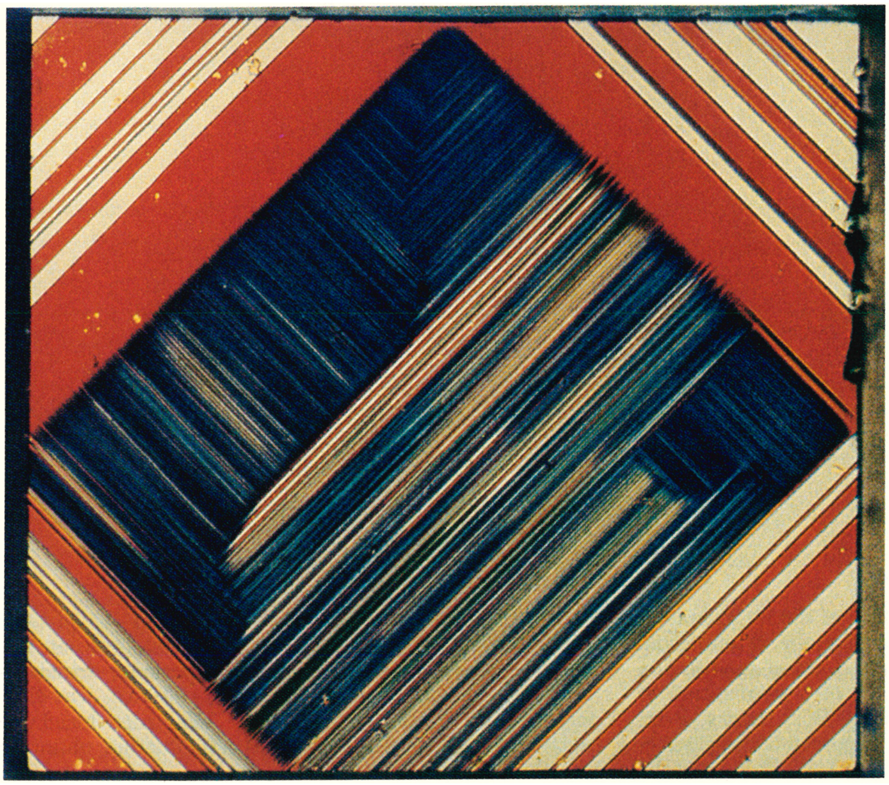


A single crystal of the superconducting layered-cuprate ceramic $YBa_2Cu_3O_{7-x}$, whose critical temperature is 92 K. The crystal, about 200 microns on a side, was grown by Debra Kaiser at the National Institute of Standards and Technology. The diagonal striations in this polarized-light micrograph (by L. C. Smith and F. Gayle) indicate twinning structure. **Figure 1**

shortly after the historic paper by John Bardeen, Leon Coooper and Robert Schrieffer[4] appeared in 1957, when Lev Gorkov derived the Ginzburg–Landau equations from the microscopic BCS theory, thus showing the equivalence of the order parameter with the pair-condensate wavefunction.

Phys. Rev. takes center stage

After World War II a number of factors conspired to shift the center of gravity of superconductivity research toward the US and the *Physical Review*, though of course much important work continued in other countries. Helium became available commercially as a byproduct of the natural gas industry. Liquefiers built in specialized low-temperature labs were now supplemented by commercially available Collins liquefiers; that opened the field to nonspecialists. The helium isotope ^{3}He, a decay product of the tritium produced for thermonuclear weapons, became available for refrigeration below 1 K, as well as for study in its own right as a Fermi liquid with fascinating ground states.

Research proceeded along two initially separate lines of investigation. The first approach used theory to guide research and to explore new quantum phenomena in well-characterized elemental and simple alloy superconductors. The second approach involved searches for new superconductors and studies of the variation of T_c with composition. The goal of that effort was to discern a pattern in the occurrence of superconductivity. It was hoped that such a pattern would reveal the essential superconducting interactions, and that it might also lead to technologically more useful superconductors with higher critical temperatures.

The more traditional first approach depended upon a close coupling between theory and experiment, but there was as yet no satisfactory theory. Many prominent theorists, among them the creators of quantum mechanics, had tried to explain superconductivity. Bardeen's deep insight into the problem is already evident in a 1941 abstract in which he suggests that superconductivity might result from a sufficiently strong electron–phonon interaction that would temporarily cause the electrons to experience Bragg reflections from the phonon waves, thus producing large diamagnetic contributions.[5] "The germ of an idea was there, and John never ceased to be fascinated by it," wrote Conyers Herring in the Bardeen memorial issue of PHYSICS TODAY (April 1992, page 29).

The discovery of the inverse square-root dependence of T_c upon mass for the different isotopes of tin, lead and mercury in 1950, by four different groups in the US and Britain, restimulated Bardeen's intense interest in the electron–phonon interaction. Evidence for this isotope effect, predicted in a model proposed in that same year by Herbert Frohlich,[6] had actually been sought experimentally at Leiden in the 1920s, when Pb isotopes first became available. In the early 1960s it was shown that the isotope effect could vary widely, and even vanish, as a result of the retarded character of the electron–phonon interaction.

The exponential behavior of the heat capacity and thermal conductivity were suggestive of an energy gap in the density of states above the superconducting ground state. Those clues, among others, guided Bardeen, Cooper and Schrieffer to the inspired discovery of the pairing theory of superconductivity, which they published in the *Physical Review* 36 years ago.[4]

Directly thereafter *Physical Review* and *Physical Review Letters* published a whole raft of papers that used the BCS theory to account quantitatively for a variety of observations, including the heat capacity anomalies, the Meissner effect, persistent currents, the temperature dependence of the penetration length, and other thermal, optical and acoustic properties. A particularly pleasing aspect of the theory was the significant role of the coherence factor in negating the effect of the large density of states in acoustic, but not electromagnetic, attenuation.

Two independent measurements of the magnetic flux quantum in 1961 provided another nice verification of the pairing theory.[7] Long before the BCS theory, Fritz London had predicted that if the superconducting wavefunction is to be single-valued, magnetic flux must be quantized in multiples of h/q, where q is the charge of the electron. The experiments found the flux quantum to be just half that predicted by London, indicating that the relevant charge unit is that of a *pair* of electrons. This important result is true for all the known superconductors, including the high-temperature superconducting cuprate ceramics discovered in the 1980s. (See figure 1.)

Tunneling

Ivar Giaever was inspired to look for evidence of the energy gap in the excitation spectra of superconductors by studying quantum tunneling through barriers. Tunneling was first proposed by Robert Oppenheimer in 1928, to account for the field ionization of atomic hydrogen. Leo Esaki's invention of the semiconducting tunnel diode demonstrated that quantum tunneling was not only interesting physics but also that it could be the basis for technologically important devices. Giaever found direct evidence for the gap in the nonlinear current–voltage curves he measured for tunneling through Al_2O_3 barriers obtained simply by allowing aluminum to oxidize in air.[8]

For superconductors with strong electron–phonon coupling, William McMillan and John Rowell at Bell Labs in 1965 used the BCS theory to develop a tunneling spectroscopy that demonstrated unequivocally that the attractive pairing interaction was mediated by phonons in all known superconductors. This is still true, except for heavy-fermion superconductors such as UPt_3, which have more exotic pairing mechanisms, and for the high-T_c cuprate ceramics, where the issue remains unclear. Unfortunately, technical details have thus far prevented the fabrication of good tunnel junctions from the high-T_c cuprates.

In 1962, thinking about the possibility of paired electrons tunneling through a barrier, Brian Josephson predicted the unusual dc and ac properties and quantum interference effects that came to bear his name.[9] Pair tunneling was regarded as improbable until Rowell and Philip Anderson experimentally confirmed Josephson's predictions.[10] (See figure 2.) Interference between two parallel superconducting tunnel junctions, which is analogous to double-slit optical interference, was first observed by scientists at Ford.[11] They introduced the acronym SQUID for this new superconducting quantum interference device.

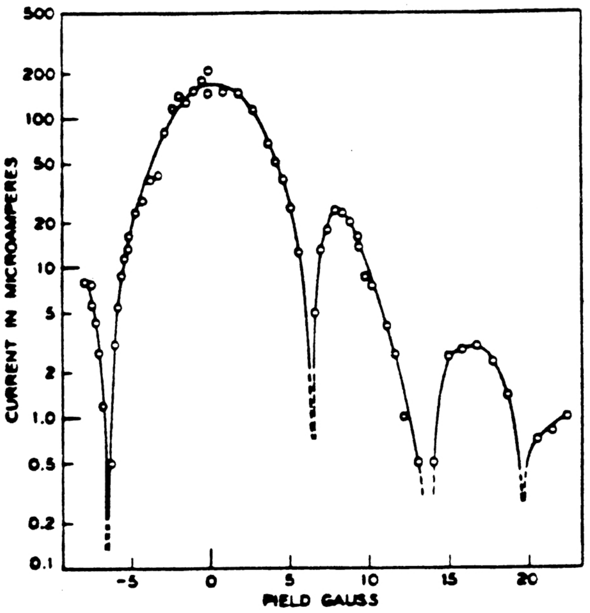
Technology for superconducting high-speed computing was developed at IBM, which eventually abandoned the effort, in part because of the materials limitations of the Pb alloy used for electrodes. Ironically, that was just when new techniques were being developed for producing more rugged and satisfactory $Nb/Al/Al_2O_3/Nb$ Josephson tunnel junctions. Nowadays these junctions form the basis of commercial Josephson-junction detectors, magnetometers, mixers, switches and voltage standards. SQUID arrays are even being used to study noninvasively the magnetic signals from neurons firing in the brain.

Searching for new superconductors

The second approach to the understanding of superconductivity after World War II involved a search for new families of superconductors. Such an approach was necessarily empirical. Bernd Matthias and John Hulm pioneered this enterprise in the early 1950s. Extensive investigations in this spirit led to the discovery of about a thousand new superconductors. Of course the most spectacular payoff of this approach came three decades later, with the discovery of superconductivity in the layered cuprates by Georg Bednorz and Karl-Alex Müller at IBM Zurich.[12]

Many interesting binary metal–metalloid compounds were found in the years before the Bednorz–Müller discovery, particularly those, such as V_3Si and Nb_3Sn, that have cubic A15 structure and therefore linear arrays of nonintersecting transition metal atoms.[13] The highest superconducting transition temperatures known at the time (above 20 K) were found in this family. NbTi, a simple body-centered cubic alloy, has become the workhorse of present-day magnet technology.

Matthias found a useful rule that qualitatively predicts, simply from the average number of valence electrons per constituent atom, whether or not a given alloy or binary compound will exhibit superconductivity.[14] Observed exceptions to the rule turned out to be signals of either new physics or unexpected materials science. Ex-



Josephson pair tunneling. This plot of critical current across a Josephson junction vs magnetic field is from the 1963 *Physical Review Letter* by John Rowell that reported the first convincing proof of pair tunneling.[10] The decrease of the critical current by three orders of magnitudes at specific small field values, as predicted by Brian Josephson, eliminated the possibility that the current was simply being carried across the junction by superconducting short circuits. **Figure 2**

amples include the dramatic reduction of T_c by scattering off magnetic impurities that violates time-reversal symmetry and breaks pairs.

It was an unexpected, pleasant surprise in 1961 when Eugene Kunzler and coworkers at Bell Labs found that Nb_3Sn samples would support large supercurrents, exceeding 150 kiloamps, in strong magnetic fields (8.8 tesla).[15] (See figure 3a.) It had taken 50 years to discover real materials that had the critical currents and fields necessary for making useful magnets and electric power machinery. It would be another two decades before the physics and materials science were understood well enough for practical production of long multistrand cables that could be wound into coils for large, powerful magnets or rotating machinery. (See figure 3b.)

In the Soviet Union, experimental work by Lev Shubnikov had already stimulated Alexei Abrikosov in 1957 to extend the Ginzburg–Landau theory to include systems in which the interface energy between normal and superconducting regions is negative.[16] Abrikosov predicted a new state, now known as type-II superconductivity, in magnetic fields above the Meissner critical field. The implications of Abrikosov's work were not pursued at the time because, I believe, the two paths being followed in the study of superconductivity in those days were decoupled from each other. Nb_3Sn research was, in fact, sometimes referred to as "schmutz physics." (*Schmutz* is German for dirt.)

Abrikosov's model is a reversible thermodynamic description that says nothing about the pinning of the flux lines needed to account for high critical currents in high fields. Charles Bean's critical-state model[17] accounts for the current flow pattern by positing that each volume element carries either its maximum critical current or no current at all.

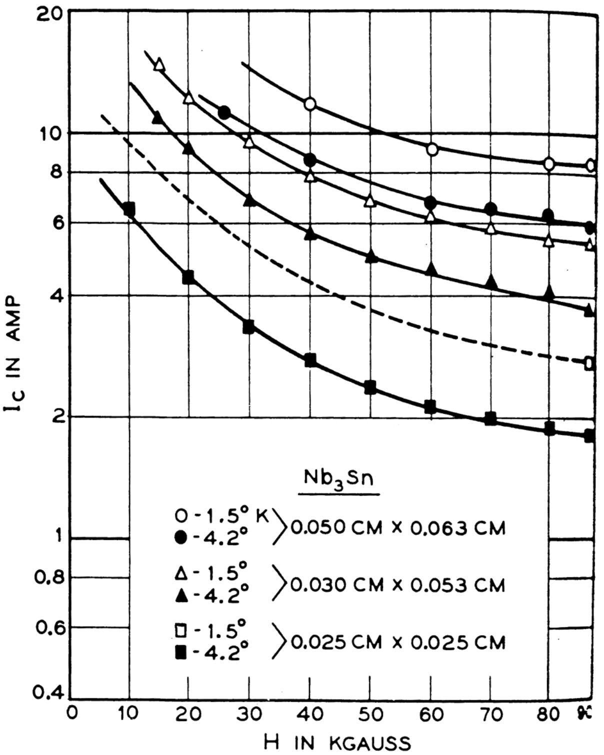
In 1962 Young B. Kim and coauthors and Anderson[18] introduced the concepts of flux creep and flux flow. After that the studies became interdisciplinary, because metallurgical defects such as precipitates, dislocations, voids, grain boundaries, surfaces and interfaces serve as flux-pinning centers. All these imperfections present spatial variations of free energy that prevent flux quanta from responding to the Lorentz force and causing dissipation. Flux-jump instabilities resulting from mechanical or electromagnetic fluctuations can lead to catastrophic quenching of the stored magnetic field energy. These instabilities were brought under control largely through research impelled by the high-energy physicists' need for big, powerful magnets for accelerators and particle detectors.

Nowadays large coils of superconducting composite wire capable of safely carrying kiloamp currents are readily available. A 1-mm-diameter high-current wire contains as many as 10^5 filaments of NbTi with a fine precipitate of hexagonal Ti that provides the pinning centers. Last year NbTi wire was used to construct more than \$1 billion worth of clinical magnetic resonance imaging systems. The wire is ready for other technologies, such as magnetic energy storage, rotating machinery and levitated trains, if and when the markets develop. The Superconducting Super Collider and CERN's proposed Large Hadron Collider would be inconceivable without NbTi superconducting magnets.

High-temperature superconductors

Bednorz and Müller's discovery of superconductivity above 30 K in ternary perovskite-related cuprate structures[12] was soon followed by the discovery of superconductivity above 90 K by Paul C. W. Chu and his colleagues at the Universities of Houston and Alabama, in a ceramic that turned out to be the layered compound $YBa_2Cu_3O_7$. This discovery of superconductivity above the boiling temperature of nitrogen generated enormous excitement and research challenges that are still at the forefront of physics. (See, for example, the June 1991 special issue of PHYSICS TODAY on high-temperature superconductivity.)

Since the pioneering work of Bednorz and Müller, a rather large family of layered copper oxide superconductors with complicated unit cells has been discovered. The parent compounds are Mott insulators with properties that are not understandable in terms of the conventional one-electron theory that has been so successful in explaining metallic, semiconducting and insulating behavior in most materials. With small changes in composition, these insulators can be doped to form conductors in which the carriers are highly correlated. In addition to their spectacular superconductivity, they also have unusual normal-state properties. All the evidence indicates that the action is on the doped CuO_2 planes. The conventional electron–phonon interaction does not suffice to explain the superconductivity of these materials, but there is as



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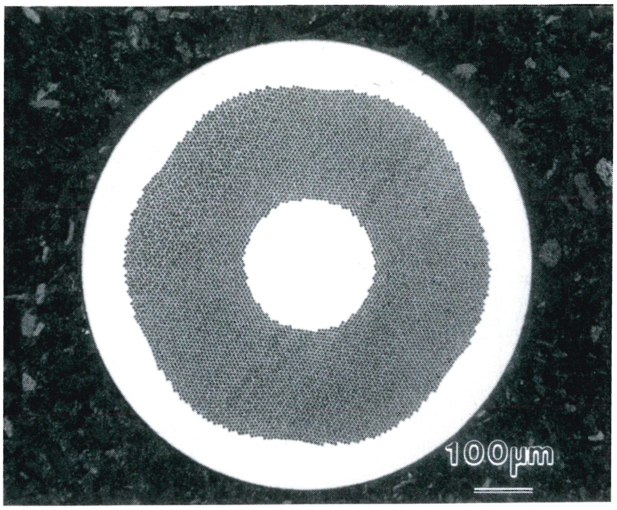

b

Niobium superconductors have critical currents and fields high enough to make them useful for large, powerful magnets. **a:** Plots of critical current vs magnetic field for short Nb_3Sn samples of various cross sections at different temperatures, from the 1961 *Physical Review Letter*[15] announcing the discovery of high-current superconductivity in very high magnetic fields. **b:** After three more decades of development we have Nb–Ti cable for the 6.6-tesla magnets of the Superconducting Super Collider. The micrograph shows the cross section of a strand 0.8 mm in diameter, fabricated at the University of Wisconsin. Each strand consists of many individual superconducting filaments, 6 microns thick, embedded in a copper matrix. (Courtesy of David Larbalestier.) **Figure 3**

yet no consensus as to the microscopic origin of the electron pairing interaction. Nowadays, new models are proposed in almost every issue of *Physical Review B* and *Physical Review Letters*.

There is, of course, a much larger potential market for devices that can operate at liquid nitrogen temperatures than for those that need liquid helium. Electronic and electrical power technologies based on the superconducting cuprates are expected to grow rapidly in the near future. SQUID magnetometers operating at 77 K have already been used to make magnetocardiograms. Simple 77 K SQUIDs are now available commercially. Signal-to-noise ratios in magnetic resonance imaging and in communications technology can be increased significantly by the use of superconducting detector coils and filters. The detection of magnetic anomalies associated with petroleum deposits and other geological features can benefit from liquid-nitrogen-cooled superconducting gradiometers. There are potentially large markets for superconducting oscillators, antennas and multichip interconnections. Possibilities for power transmission lines are bright, but they will require further study of dissipation processes.

The history of superconductivity, so much of which is to be found in the volumes of the *Physical Review* and *Physical Review Letters*, teaches us that the new quantum phenomena of today may well become the new technology of tomorrow. Presumably we won't have to wait as long for the tomorrow of liquid nitrogen superconducting technology as we did for the helium-based superconducting technology of today.

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