ELECTRONIC PAIRING IN EXOTIC SUPERCONDUCTORS

Superconductivity in heavy-fermion materials and high-T_c cuprates may involve electron pairing with unconventional symmetries and mechanisms.

Daniel L. Cox and M. Brian Maple

DANIEL COX is a professor in the department of physics at Ohio State University, in Columbus. BRIAN MAPLE is the Bernd T. Matthias Professor of Physics at the University of California at San Diego.

Investigations of rare earth, actinide, organic and oxide compounds have yielded several new classes of exotic superconductors. These include magnetically ordered superconductors, A15 superconductors, buckyball superconductors, heavy-electron superconductors,[1] organic superconductors and high-T_c oxide superconductors.[2] These materials have properties significantly different from those of conventional superconductors such as Al and Zn, which are described well by the Bardeen–Cooper–Schrieffer model of superconductivity. We carefully distinguish between the BCS model and the more general BCS theory. In the BCS theory superconductivity arises, loosely speaking, from electron pairs that behave essentially as bosons and undergo macroscopic condensation to the lowest energy state at the critical temperature T_c. The BCS *model*, presented in 1957, further specifies that the pairing is mediated by exchange of quantized lattice vibrations (phonons) between the electrons, yielding pairs with zero spin S (spin singlet) and zero angular momentum L (s wave). This model is but one example of the BCS pairing theory; another describes the superfluid state of ^{3}He, where the fermionic ^{3}He atoms form p-wave ($L = 1$) spin-triplet ($S = 1$) pairs held together by the exchange of magnetic excitations of the surrounding atomic sea.

Figure 1 shows a striking symptom of exotic superconductivity: the variation with temperature of the nuclear spin relaxation rate $1/T_1$. The rate $1/T_1$ measures the low-frequency spectrum of electronic spin fluctuations, and below T_c this spectrum is modified by the electron pairing. Below T_c, Al shows initially enhanced $1/T_1$ values; in contrast many of the exotic superconducting materials show *no* enhancement of the relaxation. Moreover, for Al, $1/T_1$ exhibits exponential behavior at low temperatures, while many exotic superconductors have a significant range of power-law behavior in $1/T_1$ below T_c.

There is no question that in all of the exotic materials some form of electron pairing takes place that can be described with the general BCS theory. At issue is whether exotic superconductivity differs from the original BCS model, in which the nodeless pair wavefunction has the same symmetry as the lattice. Proposed exotic pair wavefunctions have spatial and possibly temporal nodes that can produce novel excitation spectra capable of explaining, for example, the $1/T_1$ data of figure 1. For the exotic materials we ask:

▷ Is the pairing mediated by magnetic or other electronic excitations? (Exotic mechanism?)

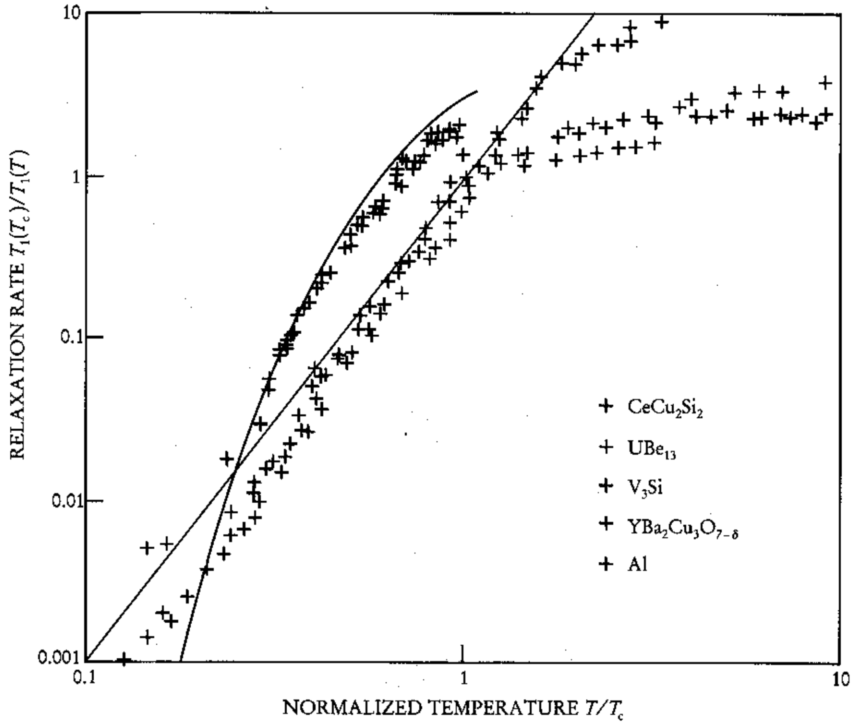
▷ Is the symmetry of the pair wavefunction lower than the symmetry of the lattice? (Exotic symmetry?)

▷ If the symmetry is exotic, does the superconducting transition induce further breaking of crystalline or time-reversal symmetry?

We shall focus on the heavy-fermion and high-T_c copper oxide (cuprate) superconductors. Although there has been no smoking-gun proof, numerous pieces of circumstantial evidence combined with heuristic theoretical arguments make a compelling case that these materials have pairs with exotic symmetry bound by nonphonon "glue."

Materials basics: Strong correlations

The high-T_c cuprate superconductors (such as $(La_{1-x}Sr_x)_2CuO_4$ and $YBa_2Cu_3O_{7-\delta}$) and the heavy-fermion superconductors ($CeCu_2Si_2$, UBe_{13}, UPt_3, URu_2Si_2, UPd_2Al_3 and UNi_2Al_3) are metallic compounds with com-



REDUCED SPIN-LATTICE RELAXATION RATES for a conventional superconductor (Al) and some exotics. The exotics shown here all have rates close to the $(T/T_c)^3$ line (blue), while that of Al is enhanced below T_c by the singular density of states and is exponential at very low temperatures (black line). FIGURE 1

plex crystal structures that reflect their multiatom unit cells. Most of the heavy-fermion superconductors are U based, a phenomenon we will call "Ubiquity." Compounds such as La_2NiO_4, $LaCu_2Si_2$ and $ThBe_{13}$ that have analogous structures but lack the appropriate Cu, Ce or U ions usually fail to superconduct.

The cuprate and heavy-fermion materials all possess strong electronic correlations. The Cu^{2+} ion has a partially filled 3d electron shell with a single hole and a cost in Coulomb energy of about 10 eV to add an additional electron; the Ce^{3+} ion has a single 4f electron with a Coulomb energy of about 6 eV; the U ion has two or three 5f electrons with a Coulomb energy of 3–4 eV. By "strong correlations" we mean that the average interaction energy substantially exceeds the average kinetic energy of these d and f states. (Electron motion through these orbitals arises from hopping to weakly correlated orbitals on surrounding ions—for example, oxygen p orbitals in the cuprates and beryllium s and p orbitals in UBe_{13}.) Approximations that treat the Coulomb interactions as weak give a very accurate description of the electronic structure in Al. Such approximations fail to describe the strongly correlated materials.

The strong correlations give rise to interesting normal-state phenomena. First, the ions with localized orbitals develop localized magnetic moments that are large and can produce antiferromagnetic order. In La_2CuO_4, for example, where the Cu has an effective magnetic moment $\mu_{\rm eff}$ of approximately two Bohr magnetons ($2\mu_B$), nearly two-dimensional antiferromagnetism occurs below a Néel temperature T_N of 240 K with an ordered moment of about $1.2\mu_B$. In UPt_3, where the U moments also have $\mu_{\rm eff} \approx 2\mu_B$, antiferromagnetism sets in below $T_N = 5$ K but is much weaker, with an ordered moment of about $0.01\mu_B$. In several heavy-fermion materials antiferromagnetism coexists with superconductivity; this does not occur in the cuprates.

Second, there is a tendency in these materials toward localized (insulating) electronic states. In La_2CuO_4, naive electron-counting arguments and conventional electronic structure theory predict a metallic ground state. Instead, the Cu^{2+} Coulomb repulsion induces an insulating ground state, and doping with Sr^{2+} for La^{3+} adds holes to the oxygen p bands and induces superconductivity. (See figure 2.) Doping nominal Ce^{4+} for Nd^{3+} in Nd_2CuO_4 donates electrons, and based on Hall coefficient measurements electrons appear to be the carriers responsible for the superconductivity. However, the correspondence of the sign of the Hall coefficient to carrier charge is not rigorous here.

A separate measure of the degree of localization is the effective mass m^* of the electron, which measures the inertial mobility of electrons. In the heavy-fermion materials, the electrons develop masses 100–1000 times the free electron mass. One can measure the effective mass through the linear (in temperature) coefficient of the electronic specific heat $\gamma = C_{\rm el}/T$, which is proportional to m^* and to the electronic density of states $N(0)$ at the Fermi energy E_F. In Al, $m^* \approx m_e$ and $\gamma \approx 1$ mJ/moleK^2; in UBe_{13} γ is 1000 times larger. Alternatively, it may be said that the effective Fermi temperature T_F of the heavy-fermion materials is of order 10 K, compared with 10^4 K in Al. We note that $T_c/T_F \approx 0.01$–0.1 for both heavy-fermion and cuprate superconductors, while $T_c/T_F \approx 10^{-4}$ in Al.

These enormous m^* values are widely believed to

Further Reading

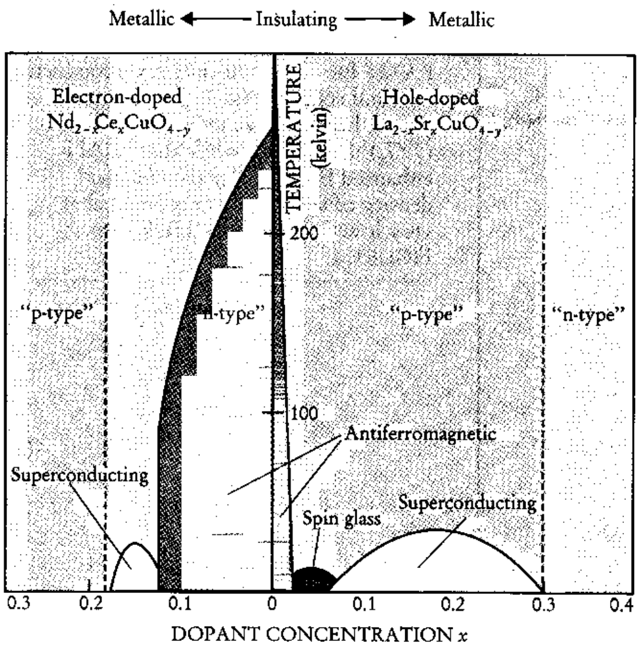
The following PHYSICS TODAY articles give more details on the indicated topics:

▷ Magnetically ordered and heavy-fermion superconductors: Maple, March 1986, page 72.

▷ Superconducting buckyballs: Arthur F. Hebard, November 1992, page 26. Although a consensus is emerging that phonon-mediated pairing occurs in buckyballs, their properties are not understood comprehensively in a strong-coupling extension of the BCS model.

▷ Organic conductors and superconductors: Paul M. Chaikin and Richard L. Greene, May 1986, page 24.

▷ High-T_c superconductors: June 1991 special issue. See also the news stories of March 1990, page 20, and May 1993, page 17.



TEMPERATURE-DOPANT CONCENTRATION PHASE DIAGRAM for hole-doped $La_{2-x}Sr_xCuO_{4-y}$ (right) and electron-doped $Nd_{2-x}Ce_xCuO_{4-y}$ (left). "Antiferromagnetic" refers to the ordering of the Cu^{2+} ions. (Adapted from C. C. Almasan, M. B. Maple, in *Chemistry of High Temperature Superconductors*, C. N. R. Rao, ed., World Scientific, Singapore, 1991, p. 205.) FIGURE 2

derive from the Kondo effect, in which an antiferromagnetic Heisenberg exchange coupling J of local moments to conduction electron spins results in the formation of a many-body resonance in the vicinity of the Fermi energy. In the heavy-fermion materials J arises from "superexchange" mediated by virtual electronic charge fluctuations on the Ce and U sites. The simple one-channel picture described in the box on page 35 is known to give an excellent description of the specific heats of alloy systems such as $La_{1-x}Ce_xPb_3$ over the whole range $0 \leq x \leq 1$ (see the review article by Patrick A. Lee and colleagues[1]), and is supported by a number of theoretical studies of the concentrated Kondo lattice model.

In the strong-coupling limit ($J \geq E_F$), the Kondo effect has been used to develop a model for low-energy excitations of the cuprates. In the Zhang–Rice mapping, introduced by Fu-Chun Zhang and T. Maurice Rice,[3] a single hole, prohibited by the Coulomb interaction from residing on the copper site, goes onto oxygens (as seen experimentally) and antiferromagnetically binds into a local singlet with the copper hole spin. As oxygen holes move, the singlet is transported between copper sites, and this motion appears equivalent to the motion of a copper hole. The effective mass of these singlets is only 2–4 times free-electron band masses.

It is generally accepted that to explain the exotic superconductivity we must understand the highly unusual normal states.[2] In the cuprates, attention has been drawn to the non-Fermi-liquid character of the normal state. That is, the low-lying electronic excitations apparently lack the 1:1 mapping to a gas of noninteracting electrons seen in the Landau Fermi-liquid theory for ^3He and simple metals. In Landau theory, the low-lying excitations of the interacting system are described by quasiparticles, that is, electrons dressed by clouds of other excitations. The validity of the quasiparticle concept requires that the quasiparticles' decay rate vanish quadratically with decreasing temperature and energy (relative to E_F); concomitantly, $\gamma(T)$ remains approximately constant. In metals, this quasiparticle decay rate may be sampled by the electrical resistivity. In contrast to the Landau theory, the resistivity varies linearly with temperature as $T \to 0$ in the cuprates; that is, the average decay width of the low-lying charge excitations is comparable to their average energy. For the heavy-fermion materials, resistivities quadratic in T are sometimes observed (as in UPt_3) but not always (as in UBe_{13}). Moreover, $\gamma(T)$ still increases with decreasing T in UBe_{13} and $CeCu_2Si_2$. A number of related alloys (such as $Y_{1-x}U_xPd_3$ and $Th_{1-x}U_xRu_2Si_2$) have been found for which[4] $\gamma(T) \propto -\ln T$. Since the Fermi-liquid paradigm underlies the conventional theory of superconductivity, great conceptual advances may be required to explain the pairing transitions in these materials.

BCS pairing theory and model

To set the context for understanding exotic superconductivity, we first briefly review the BCS theory and model.

When electron–electron interactions are present, pairing is assumed to take place between Landau quasiparticles rather than between electrons in noninteracting energy bands. Nevertheless one still talks of "electron pairs." In the BCS theory, the pairing of electrons and condensation of pairs with zero center-of-mass momentum occur at precisely the same temperature: T_c. However, rather than performing a "tango" in the superconducting state, the electron pairs participate in a "square dance," exchanging partners on a time scale of order $\tau_c = \hbar / k_B T_c$. The characteristic separation of pairs is the coherence length $\xi = v_F \tau_c$ (where v_F is the Fermi velocity), which is of order 1000 Å in Al, and 15 Å in $YBa_2Cu_3O_{7-\delta}$. Below T_c the electron-pair wavefunction Ψ has nonzero amplitude and serves as an order parameter analogous to the spontaneous magnetization of Fe below the Curie temperature.

The pair wavefunction has symmetry properties constrained by the Pauli principle, which demands that the wavefunction change sign under exchange of spin and orbital labels. In the absence of spin–orbit coupling and neglecting crystalline anisotropy, we classify the pair wavefunctions by the center-of-mass angular momentum **L** and spin **S**. Electron pairs in a spin-antisymmetric state ($S = 0$) may have any even L value (even parity), assuming the pair wavefunction is even under reversal of frequency. Spin-symmetric ($S = 1$) pairs may have any odd L value (odd parity).

For weakly correlated materials such as Al simple energetics dictates that the isotropic spin-singlet state ($L,S = 0$) will be favored. This is because the total energy is dominated by the positive kinetic energy, which is lowest when Ψ has the fewest nodes. Such a pair wavefunction is described by a single complex number.

Quasiparticle pairing reduces the excitation density of states $N(E)$ near E_F relative to the normal state. This reduced excitation density stabilizes the superconducting state. The reduction occurs because the pairs all go into a wavefunction with the same phase when they condense. The phase ϕ is conjugate to the electron number N_e, in the same sense that position and momentum are conjugate variables, and thus they obey an uncertainty relation $\Delta\phi\, \Delta N_e \approx 1$. In the normal state there is no preferred phase, because electron number is precisely conserved. The superconducting condensation that makes $\Delta\phi$ small requires ΔN_e to be large to satisfy the uncertainty relation, and charge conservation no longer holds for the superconducting sample (described as part of a grand canonical ensemble). (Electromagnetic gauge symmetry is also broken for the superconducting subsystem.) As a consequence, occupied (particle) states mix with unoccupied (hole) states. Above T_c particle and hole energy levels cross at E_F in all momentum ($\mathbf{k}$) directions. Below T_c the particle–hole hybridization will thus induce a gap at each such point of the Fermi surface, except possibly at special $\mathbf{k}$ values for which symmetry might force the mixing matrix element to vanish. The gap function $\Delta(\mathbf{k})$ is proportional to the Fourier transform of the electron-pair wavefunction $\Psi(\mathbf{r})$ and has a maximum value of order $k_B T_c$. Hence, for nearly uniform $\Psi(\mathbf{r})$ (s wave) a nearly isotropic $\Delta(\mathbf{k})$ results. Figure 3 shows sketches of some $\Delta(\mathbf{k})$ and $N(E)$ possibilities relevant to the cuprate superconductors.

One probe of low-energy electronic excitations is the spin–lattice relaxation rate $1/T_1$ measured in nuclear magnetic resonance ($1/T_1$ is the rate at which induced nuclear magnetization decays as a result of spin exchange with electrons in the material). Because nuclear magnetic moments are small, a nuclear spin flip requires negligible energy (about 10^{-7} eV in a 1-T field). In the normal state, a spin flip will scatter an electron from a hole state to a particle state. The rate $1/T_1$ then goes as the product of the particle and hole densities of states times the width of the overlap region of occupied- and unoccupied-state Fermi functions, which is of order $k_B T$ in the normal state. Hence we expect $1/T_1 \propto T$ in the normal state. (Deviations from this Korringa law occur in the cuprate superconductors, depending on the nucleus studied.) Below T_c the Fermi-function overlap is exponentially suppressed for a constant gap function Δ, so that $1/T_1 \propto \exp(-\Delta/T)$. There is also a significant enhancement of $1/T_1$ below T_c due to the square-root singularity in the excitation density of states at the gap edge (see figure 3). Observation of this "coherence," or Hebel–Slichter, peak in Al (see figure 1) gave considerable support to the BCS model.

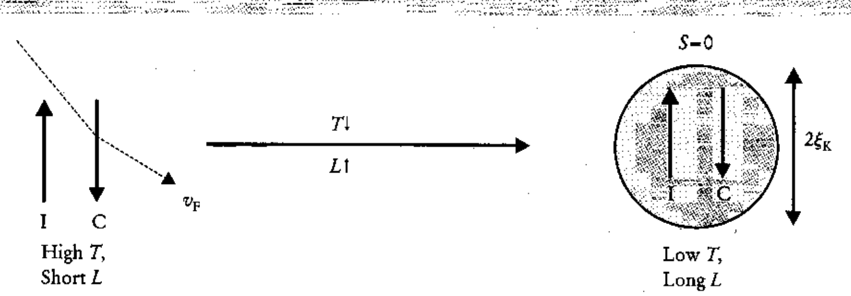
Since electrons repel in free space, the pairing "glue" must arise from the solid state. The BCS model assumes that virtual exchange of phonons mediates the electron attraction. The well-known picture is that an electron moving through the lattice virtually polarizes the posi-

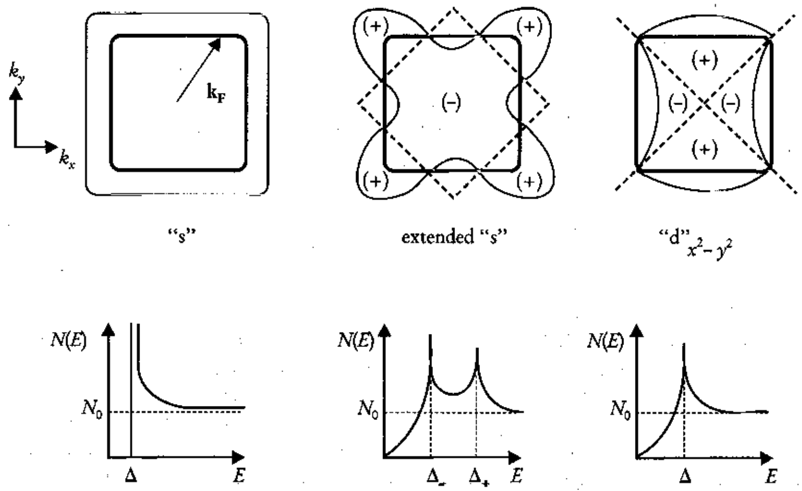
Kondo Effect

The Kondo effect involves an antiferromagnetic Heisenberg exchange coupling J of local moments of impurities to conduction electron spins. Jun Kondo in 1963 used this effect to explain resistivity minima in metals with dilute concentrations of local moments. By calculating the scattering rate of electrons perturbatively to the third order in $|J|/E_F \ll 1$, Kondo showed that the effective exchange coupling for a lone magnetic ion grows logarithmically as the temperature is lowered. Successive terms in the perturbation theory expansion grow to equal size at the Kondo temperature T_K, given approximately by $k_B T_K \approx E_F \exp(-E_F/|J|)$.

The superficial low-temperature divergence of the effective coupling strength at T_K was the first and perhaps simplest example in physics of "asymptotic freedom," the same principle that emerged from the Yang–Mills theories at the heart of the standard model of particle physics.

Nonperturbative treatments of the Kondo effect, the first of which was the numerical renormalization-group approach of Kenneth G. Wilson, showed that the logarithmic divergence is halted and a many-body singlet ground state is formed with effective exchange coupling that is indeed infinite at $T = 0$. The singlet "lump" forms as temperature T is lowered and length scale L is increased, and has spatial extent of about $\xi_K = \hbar v_F/k_B T_K$. (See illustration; "I" denotes the impurity local moment and "C" denotes a conduction electron.) The excitations surrounding the lump can be described as a Landau Fermi liquid, with a 1:1 map to the excitations of the noninteracting system and an effective Fermi temperature $T_F \approx T_K$ (that is, $\gamma(T) \approx 1/T_K$ per impurity).[1]





FERMI-SURFACE GAP FUNCTIONS AND DENSITIES OF STATES of a superconductor with tetragonal symmetry for various pairing symmetries. The gap functions in the $k_z = 0$ plane (top) are represented by the blue lines; distance from the Fermi surface (black lines) gives the amplitude, a positive value being outside the Fermi surface, a negative value inside. The corresponding density of states for one-quasiparticle excitations $N(E)$ is shown below each gap function, with N_0 the normal-state value. Gap node surfaces are represented by the dashed lines. Left: The classic s-wave case, where the gap function is constant, with value Δ. This gives rise to a square-root singularity in $N(E)$ at energy $E = \Delta$. Middle: The extended-s-wave case derives from pairs situated on nearest-neighbor square lattice sites in real space, with an approximate k-space form of $\cos(k_x a) + \cos(k_y a)$. For the Fermi surface shown here, the gap function has lines of nodes running out of the page. Right: A d-wave function of $x^2 - y^2$ symmetry. The extended s-wave and d-wave functions shown here each have a linear density of states up to order Δ, which measures the maximum gap amplitude about the Fermi surface. FIGURE 3

tively charged ionic background, which in turn attracts another electron moving through at a later time. The characteristic length scale for this interaction is small, on the order of a lattice spacing. However, the characteristic time scale—the interval before one electron passes through a region polarized by its partner—is long, of order $1/\omega_0 \gg 1/E_F$, where ω_0 is the maximum vibrational frequency of the lattice. This temporal separation effectively reduces the Coulomb repulsion.

The BCS theory predicts a simple exponential relation between T_c and the net attractive interaction strength V. Taking the normal-state Fermi-energy density of states to be $N(0)$ and the time-averaged Coulomb repulsion to be U^*, T_c is given by

$$k_B T_c \approx 1.13\hbar\omega_0 \exp\left(\frac{1}{N(0)\,[V - U^*]}\right) \qquad (1)$$

From this equation we learn:

▷ An arbitrarily weak net attraction ($V - U^* < 0$) will yield superconductivity.

▷ T_c is exponentially sensitive to input values of model parameters, rendering any T_c estimate accurate only to within an order of magnitude.

▷ Naively, $T_c \propto \omega_0 \propto M^{-1/2}$, where M is the mass of the atoms forming the lattice. By use of isotopic substitution, which doesn't alter the electronic structure, this square-root dependence was indeed seen for simple superconductors prior to BCS and helped motivate the BCS work. For superconductors in which the dynamical nature of the phonon-mediated attraction must be taken fully into account (the strong-coupling limit), U^* acquires a dependence on M, because the time scale for U^*'s averaging is $1/\omega_0$. In those cases it is possible to find $T_c \propto M^{-\alpha}$ with $\alpha \approx 0$ or even $\alpha < 0$.

Beyond the BCS model: Experimental evidence

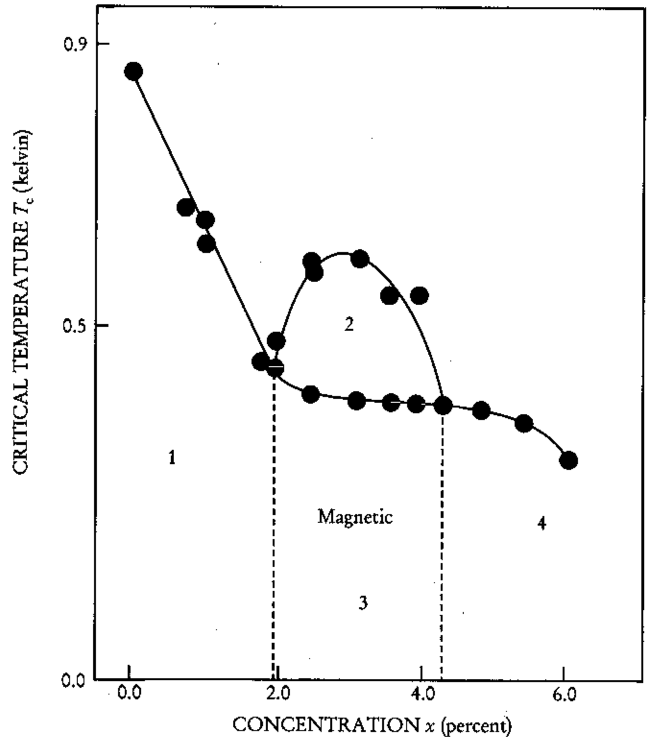
We now survey properties of the cuprate and heavy-fermion superconductors that appear to go beyond the BCS model.

Unusual excitation spectrum. We focus here on $1/T_1$. In contrast to the behavior of Al, for the heavy-fermion and cuprate superconductors we see in figure 1 a drop in $1/T_1$ below T_c and power-law behavior (proportional to T^3) well below T_c. Such power laws are ubiquitous for the heavy-fermion superconductors, showing up in measurements[1] of specific heat, ultrasound attenuation and London penetration depth $\lambda(T)$. The London penetration depth measures the length at which an external magnetic field is fully attenuated by the diamagnetic screening of the superconducting state. The cuprate superconductors show power-law behavior in $1/T_1$, London penetration depth[5] and nuclear Knight shift[2] (the shift in energy of a nuclear spin due to the presence of the conducting electrons).

Complicated phase diagrams. In the alloy system $U_{1-x}Th_xBe_{13}$, there appear to be four distinct superconducting phases in the T–x (temperature–dopant concentration) plane.[6] (See figure 4.) One can describe this phase diagram with two distinct pair-wavefunction amplitudes Ψ_1 and Ψ_2, with Ψ_1 nonzero in regions 1, 3 and 4, and Ψ_2 nonzero in regions 2 and 3. This interpretation is strongly supported by pressure experiments.[7] In region 3 the superconducting phase has an associated spontaneous magnetization, as determined by implantation of positive muons, which sample the local internal fields.[6] Thus the superconducting state breaks time-reversal symmetry, since the induced magnetization reverses direction under time reversal. UPt_3 shows similarly rich phase diagrams in applied magnetic field at ambient pressure and in applied pressure at zero field.[8]

Proximity of local-moment magnetism. As discussed earlier, local-moment magnetism (usually antiferromagnetism) and superconductivity are in close proximity

PHASE DIAGRAM for $U_{1-x}Th_xBe_{13}$. The four superconducting regions (numbered) can be described by two pair wavefunctions. In phase 3 there is evidence from muon spin rotation for an anomalous magnetic moment of order 0.001–$0.01\mu_B$. Colors indicate results from different experiments. (Adapted from ref. 6.) FIGURE 4



to one another in these materials. This is surprising, because local moments tend to break pairs and suppress superconductivity: In the $S = 0$ Cooper pair the spins of the paired electrons are antialigned, and the local moment tends to align these spins to minimize the exchange energy. In Zn, for example, a concentration of just a few parts per million of local moments carried by 3d-transition-metal impurities (such as Mn) drives $T_c \to 0$. In the heavy-fermion and cuprate superconductors, the local moments reside on the active sites responsible for the superconductivity. In contrast, in the rare earth (R) magnetic superconductors RMo_6X_8 (X = S, Se) or RRh_4B_4, the rare earth magnetic moments and the superconducting Mo_6X_8 and Rh_4B_4 clusters are spatially separated. (See the article by Maple in PHYSICS TODAY, March 1986, page 72.)

Small isotope effect. For the cuprate superconductors, there is (as T_c gets large) only a small isotope effect on T_c. For example, in $YBa_2Cu_3O_7$ isotopic substitution for Ba or O yields[2] no significant change in T_c. That is, α is about 0. This all but rules out phonon-mediated pairing, since it is difficult to reconcile $\alpha = 0$ from conventional theory with high vibration frequency, large U^* and relatively weak electron–phonon coupling.

Pairing anisotropy in the cuprates. Several probes appear to offer direct symmetry-based evidence for unusual pairing. (See the news story in PHYSICS TODAY, May 1993, page 17.) Because of the high T_c, gap values are large enough to be measured by photoemission spectroscopy (as has been done by Zhi-Xun Shen and coworkers), which can probe the occupied electron states as a function of direction with a resolution of ≤ 0.01 eV (or about 100 K). These measurements indicate a significant gap anisotropy, with the gap vanishing to within resolution at several points on the Fermi surface.

Unusual normal states. As discussed earlier, the normal states (that is, states above T_c) in these materials are generally highly unusual and may violate the Landau paradigm, making a straight application of the BCS pairing theory questionable. Even so, various experiments (flux quantization, Josephson junctions in microwave backgrounds) confirm that in the cuprate materials the carrier charge is twice the electron charge. Hence pairing occurs—what theoretical framework will allow us to understand that?

Symmetry considerations in exotic pairing

Exotic superconductivity may deviate from the original BCS model by having L or S different from zero. This can produce superconducting phases described by more than a single complex number. For example, for an isotropic system, the d-wave ($L = 2$) singlet state is described by five complex numbers that transform into one another under the elements of the rotation group. We shall call such pair wavefunctions "multicomponent." This multicomponent character means that at least two superconducting states are degenerate at the transition temperature. Analogous degeneracy occurs in superfluid ^{3}He, where the fermionic He atoms form pairs with $S = 1$ and $L = 1$.

In ^{3}He, as in the cuprate and heavy-fermion superconductors, there is a large local repulsion between the relevant pairing fermions. Because states with $L > 0$ introduce nodes at zero separation, thus reducing the repulsion (albeit at the cost of increasing the kinetic energy), such states are favored. Just as in Hund's rules for atoms, the energy optimization may favor $L \neq 0$ for large local repulsion, that is, for strong correlations.

Unlike what happens in an isotropic medium such as ^{3}He, however, in a crystal L and L_z cease to be good quantum numbers because of the discrete rotational symmetry. This lowers the possible degeneracy of pair states. Nonetheless, multicomponent pair states are possible and can give rise to superconducting phases that break time-reversal ($\mathcal{T}$) or crystalline symmetry.[1] In a broken-$\mathcal{T}$ phase, complex relative phases between the components generate spontaneous supercurrents and hence internal fields. For broken crystalline symmetry, the multicomponent order parameter couples to elastic strains and induces a distortion analogous to that of a cubic ferromagnet.

Exotic pairing symmetry is directly manifested in the quasiparticle excitation spectrum. For example, in the tetragonal (fourfold rotation symmetry) or nearly tetragonal crystal structures of the cuprate superconductors, if instead of s-wave pairs, d-wave pairs of $x^2 - y^2$ symmetry were developed, the gap function in $\mathbf{k}$ space would be proportional to the quadratic form $k_x^2 - k_y^2 \propto k^2 \cos 2\theta$. (See figure 3.) Note that this gap function has lower symmetry than the crystal; for example, it changes sign with fourfold rotations. Thus the gap vanishes on lines of nodes running through the Fermi surface, giving rise to power-law behavior in thermodynamic quantities that probe $N(E)$. For example, $1/T_1 \propto T^3$ for this gap function. Furthermore, the anisotropy and nodes induce a spread in gap functions, which smears out the BCS-model square-root singularities in the excitation density of states. This smearing removes the coherence peak in $1/T_1$. Despite the attractiveness of this simple picture, a consistent explanation of all power laws with a given model gap function is still not possible without additional assumptions.

Exotic pairing symmetry also possibly explains the unusual phase diagrams of UPt_3 and $U_{1-x}Th_xBe_{13}$. Knowing the symmetry properties alone allows one to write down a phenomenological Ginsburg–Landau free-energy functional that is a Taylor series expansion in powers of the pair wavefunctions and their spatial gradients. One then studies the stable phases of this free energy. In UPt_3, certain two-component pair wavefunctions allowed in the hexagonal crystal have been widely studied.[8] While the two-component wavefunction picture can explain many properties, including $\mathcal{T}$-reversal breaking in the low-temperature phase, there is controversy about whether it accounts for the phase diagram in all orientations of magnetic field.

The case for an exotic-symmetry pair wavefunction in the cuprate materials is strong. In addition to the aforementioned power laws and the gap anisotropy and apparent gap nodes observed in electron photoemission spectroscopy, recent tunneling experiments provide direct probes of the gap-function symmetry. (See the May 1993 news story.) In the "corner-SQUID" tunneling experiment of David Wollman and coworkers, a superconducting lead strip is attached around the corner ($x = y$) of an oriented single crystal of $YBa_2Cu_3O_7$ (YBCO). If there is an $x^2 - y^2$ superconducting state in the YBCO this state will, under zero external voltage or field, produce an intrinsic phase difference of π in traversing the YBCO–Pb loop. The data support this interpretation. No such behavior was seen for an edge-SQUID, in which both ends of the Pb strip were attached on one side of the crystal. However, recent experiments by A. Guoping Sun and coworkers find c-axis Josephson tunneling of electron pairs from YBCO into Pb.[9] Since Pb has an isotropic pair wavefunction, the net current from positive $x^2 - y^2$ lobes should cancel that from the negative lobes at zero applied junction voltage and magnetic field. Instead, the researchers saw a zero-voltage, zero-field supercurrent through the junction. In a nonzero field the current was modulated according to the classic Fraunhofer diffraction pattern anticipated for a conventional Josephson junction.

A resolution of these apparently conflicting data may lie in highly anisotropic "s-wave" pairing. Philip W. Anderson and Sudip Chakravarty believe that interlayer pairing will mix an s-wave pair wavefunction with high-angular-momentum states that are still invariant under crystal symmetries. (See the May 1993 news story.) Figure 3 shows such a state with a low-frequency excitation spectrum linear in energy. Alternatively, a $\mathcal{T}$-breaking superconducting state having a gap function of the form $\Delta(\mathbf{k}) = \Delta_s + i\Delta_d(\mathbf{k})$ with $\Delta_d(\mathbf{k}) \propto k_x^2 - k_y^2$ and Δ_s and Δ_d real can produce similar phenomenology and possibly explain the corner-SQUID experiment. The net wavefunction has the form $\Psi_s + i|\Psi_d|$, so the phase is called "s + id." However, such $\mathcal{T}$ breaking is unlikely, given null results from optical-rotation and muon spin-rotation experiments.

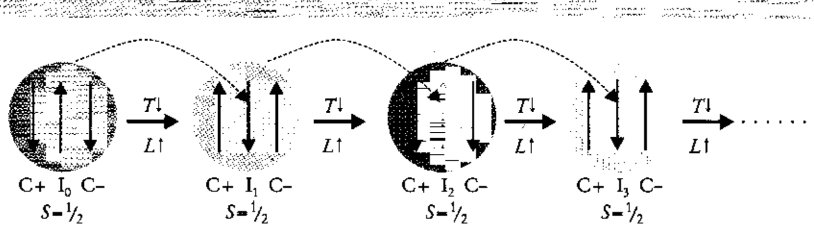
Exotic pairing mechanisms

Any pairing mechanism that does not rely upon phonon-mediated attraction is considered exotic. Because of relatively weak electron–phonon coupling and strong electronic correlations, most theorists believe that the attraction in the cuprate and heavy-fermion materials is generated within the electronic system alone. The most popular candidate mechanism in each is the exchange of antiferromagnetic spin fluctuations. Figure 5 shows two simple pictures of this mechanism and illustrates that at least two antiferromagnetic fluctuations must be exchanged to induce the attraction. In the cuprates, these excitations go out to quite high energies ω_m (of order 0.5 eV), which could explain the high T_c values, if we heuristically replace ω_0 in equation 1 by ω_m.

Two main approaches have been used to develop this idea quantitatively for the cuprates. In one, Pierre Monthoux and David Pines[10] developed a strong-coupling theory in which the dynamic electron–electron attraction is modeled using a phenomenological spin-fluctuation spectrum developed to fit nmr and neutron scattering data. This theory produces a superconducting state with $x^2 - y^2$ symmetry, a relatively high transition temperature and a gap function that grows rapidly away from the nodal regions, which helps to fit the $1/T_1$ data below T_c. Parallel efforts have been undertaken in approximate studies of the one-band Hubbard model by Chien Hua Pao and N. Eugene Bickers and by Monthoux and Douglas Scalapino.[11] In this model one electron band is retained, together with a large on-site repulsion. The origin of the band is presumed to be hybridized copper–oxygen orbitals. This model produces a spin-excitation spectrum that has been successfully employed to fit the nmr and neutron data. It

Two-Channel Kondo Model

In the two-channel spin-½ Kondo model the spin-½ local moment couples antiferromagnetically to two exactly degenerate channels of electrons ($C_\pm$), producing a new effective spin ½. That spin in turn couples to two channels on the next length scale, resulting in a self-similar picture as $T \to 0$. (See illustration.) The numerical renormalization-group approach shows that the electron cloud around the impurity has a screening length that diverges as $1/T$ when $T \to 0$. (Recall that the screening cloud had finite size of order ξ_K in the one-channel model.) The spin-triplet conduction electron pairs and the bound impurity spin mix with an odd-in-frequency pair wavefunction. The two-channel Kondo model has a non-Fermi-liquid excitation spectrum,[19] for which $\gamma(T) \approx \ln(T_K/T)/T_K$ as $T \to 0$. Hence this model represents a playground for studying the breakdown of the Landau Fermi-liquid paradigm.



is not clear, however, if there is a superconducting transition for this model in the thermodynamic limit. Exact numerical solutions of the Hubbard model (and the closely related t–J model) for small system sizes do show enhanced d-wave pairing correlations. Other excitations (such as copper-site charge fluctuations) can mediate $x^2 - y^2$ pairing, so the observation of this pair state doesn't completely determine the mechanism. Another novel approach for the cuprates involves charge-modulated hopping, which can serve to pair holes—it has been observed by Jorge Hirsch that like the "hole-doped" cuprates, a majority of elemental superconductors have positive Hall coefficients.[12]

For UPt_3, Michael Norman carried out an effort similar to that of Monthoux and Pines, taking the spin-fluctuation spectrum from neutron data. The stable pair wavefunction thus obtained had the wrong nodal structure to explain the experimental power laws.[8] Norman subsequently generalized the Hubbard model.[13] The "gluing" excitations are now local multipolar fluctuations, and the favored superconducting state for a wide range of parameters is the doublet-pair wavefunction used in many Ginsburg–Landau theory treatments.

Beyond the Landau Fermi liquid

We now turn to theories not describable in terms of pairing of Landau quasiparticles. One such theory, "anyon superconductivity," has attracted considerable interest in the last several years.[14] The concept of anyons arose first in condensed matter physics in the context of the fractional quantum Hall effect, where the wavefunction proposed by Robert Laughlin was found to describe the ground state. Laughlin's wavefunction could be viewed as a kind of Bose condensate with fractionally charged particles. The fractional charge is directly connected to "fractional statistics": In two dimensions, the exchange of two particles may give rise to a phase factor $\exp(i\theta)$, with θ taking on any value (hence "*any*ons"), in contrast to $\theta = 0$ or π for bosons or fermions, respectively. Alternatively, the Aharonov–Bohm effect causes such phase factors if magnetic tubes (infinitesimal solenoids) with flux strength set by θ are attached to physical fermions. Hence, the free-anyon model is actually a complicated many-body problem! For the cuprate superconductors, Laughlin argued that the disordered magnetic insulating phase should have $\theta = \pi/2$ fractional-spin excitations at low T, and that doping to a metallic phase unleashes $\theta = \pi/2$ charge excitations, which then pair to give superconductivity. However, subsequent work by Daniel Rokhsar suggests that the anyon superconductor wavefunction is in fact a novel parameterization of a particular $\mathcal{T}$-breaking BCS state.[15]

A different route beyond the BCS paradigm lies in consideration of pair wavefunctions that are odd under frequency inversion, which means they have a temporal node ($\omega \to \partial/\partial t$ under Fourier transformation).[16,17] Consider, for example, the spin-triplet wavefunction

$$\Psi_{\mathrm{odd},+}(\mathbf{r},t) = \psi_\uparrow(\mathbf{r},t)\,\frac{\partial}{\partial t}\,\psi_\uparrow(\mathbf{r},t) \qquad (2)$$

where $\psi_\sigma(\mathbf{r},t)$ is a one-electron wavefunction. Now the Pauli principle is satisfied even though $S = 1$ and L is even, because of the temporal node. The ease of writing $\Psi_{\mathrm{odd},+}$ is deceptive, since for appropriate models it mixes with a many-body wavefunction describing an electronic spin bound to an even-in-frequency (no temporal node) pair.

Studies of the odd-in-frequency state have recently shown that:

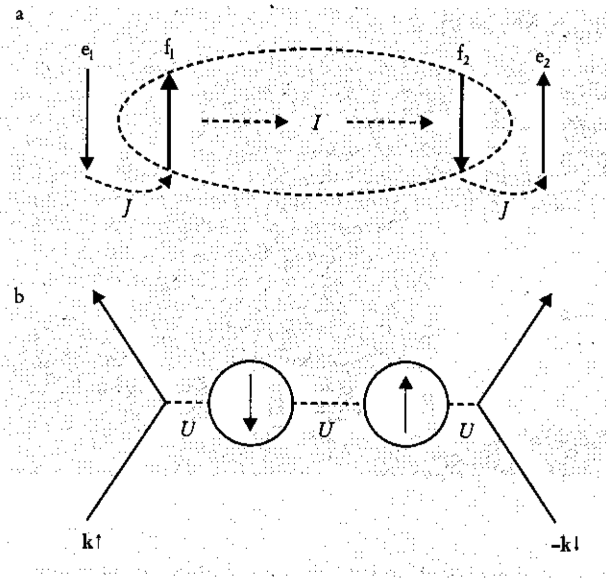
▷ The thermodynamic average of states like $\Psi_{\mathrm{odd},+}$ vanishes, though the coefficient of the short-time expansion in t may have a nonzero average and serve as an order parameter.

▷ Models developed so far appear to yield no Meissner effect for pairs with zero center-of-mass momentum. However, there are indications that odd-in-frequency pairs with nonzero center-of-mass momentum can give a Meissner effect.[18]

▷ Unless the effective pairing interaction is singular in T, a critical coupling strength of order E_F is required to induce superconductivity.

The two-channel Kondo impurity model[19] is the only one for which a tendency toward odd-in-frequency pairing is rigorously established;[17] moreover, the effective odd-in-frequency pairing interaction is singular. In this model, a spin-½ moment couples to two degenerate bands or channels of conduction electrons. (See the box above.) In a two-channel magnetic Kondo model of a Ce ion in a heavy-fermion material the channels are locally degenerate electronic orbitals. A two-channel quadrupolar Kondo model is possible for U ions in which the quantum shape fluctuations of the U ions are screened "antiferroquadrupolarly" by local orbital motion of the conduction electrons. In this case the magnetic "spin" of the itinerant states serves as the channel index.[20]

There are empirical reasons to seriously consider the two-channel Kondo model as a source of heavy-fermion superconductivity. First, all the heavy-fermion superconductors except UPt_3 show the expected $-\ln T$ behavior in $\gamma(T)$ upon substantial dilution of the rare earth–actinide



ANTIFERROMAGNETICALLY MEDIATED PAIRING in exotic superconductors. **a:** A real-space picture assuming that the mobile electrons pair through exchange of a spin fluctuation in the localized moment system. Exchange coupling J of electron e_1 to the local moment on site f_1 polarizes that moment. Through the antiferromagnetic exchange coupling I, this spin polarizes the second site f_2, making it a favorable location for another electron, e_2. Since two spin flips are involved, the process is a two-magnon one. For the cuprates the mobile carriers could be oxygen holes, and the local moments reside on copper sites. For the heavy-fermion materials the ligand atoms supply the mobile carriers, and the 4f or 5f sites supply the local moments. **b:** The momentum-space picture relevant to a single-band Hubbard model. Again, two spin polarizations are required to mediate a pairing interaction. FIGURE 5

sublattice, as does the alloy system[4] $Y_{1-x}U_xPd_3$. Second, symmetry and dynamic conditions that limit candidate materials for the two-channel Kondo effect are met in all the heavy-fermion superconductors. For Ce-based systems the conditions are severely restrictive: Only $CeCu_2Si_2$ satisfies them! However, any tetravalent U ion with a ground doublet in hexagonal, tetragonal or cubic symmetry can exhibit the quadrupolar Kondo effect, which may account for the "Ubiquity" mentioned earlier.[20]

Outlook

Clearly much remains to be learned about electron-pairing transitions in the cuprate and heavy-fermion superconductors. While the evidence for exotic pairing in terms of Cooper pairs with higher-than-s-wave angular momentum appears quite strong for both classes of materials, uniform agreement on this point has yet to be reached. Nor has an appropriate order parameter been universally settled upon in either case (although there is considerable evidence for an exotic symmetry or at least a highly anisotropic pair wavefunction in the cuprates). No smoking-gun proof of antiferromagnetic fluctuation-mediated pairing exists, although the comparison of data with approximate calculations is favorable for the cuprates. As for the truly exotic theoretical possibilities (anyons, odd-in-frequency pairs, two-channel Kondo models), further theoretical efforts are required to establish their relevance to experiment. The common features of the cuprate and heavy-fermion materials (such as the apparently anisotropic superconductivity and non-Fermi-liquid behavior) should continue to motivate extensive experimental and theoretical research efforts for many years to come.

Part of this work was written while one of us (Maple) was a visitor at the Center for Materials Science at Los Alamos National Laboratory. We would like to acknowledge research support from the Division of Materials Research of the DOE Office of Basic Energy Sciences and from the NSF.

References

1. Reviews of heavy-fermion materials include P. A. Lee, T. M. Rice, L. J. Sham, J. Serene, J. W. Wilkins, Commun. Cond. Matt. Phys. **12**, 99 (1985); L. Gorkov, Sov. Sci. Rev. **9A**, 1 (1987); N. Grewe, F. Steglich, in *Handbook of the Physics and Chemistry of the Rare Earths*, vol. 14, K. A. Gschneidner Jr, L. L. Eyring, eds., Elsevier, Amsterdam (1991), p. 343.
2. For a review see various articles in D. M. Ginsberg, ed., *Physical Properties of High Temperature Superconductors*, vols. I–III, World Scientific, Singapore (1989–92).
3. F.-C. Zhang, T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
4. C. L. Seaman *et al.*, Phys. Rev. Lett. **67**, 2882 (1991). H. Amitsuka *et al.*, Physica B **186–188**, 337 (1993).
5. W. N. Hardy, D. A. Bonn, D. C. Morgan, R. Liang, K. Zhang, Phys. Rev. Lett. **70**, 3999 (1993).
6. R. Heffner *et al.*, Phys. Rev. Lett. **65**, 2816 (1990).
7. S. E. Lambert *et al.*, Phys. Rev. Lett. **57**, 1619 (1986).
8. J. Sauls reviews the understanding of UPt_3 in terms of two-component pair wavefunctions in Adv. Phys. **43**, 113 (1994).
9. A. G. Sun, L. M. Paulius, D. A. Gajewski, M. B. Maple, R. C. Dynes, Phys. Rev. Lett. **72**, 2267 (1994).
10. P. Monthoux, D. Pines, Phys. Rev. Lett. **69**, 961 (1992).
11. C. H. Pao, N. E. Bickers, Phys. Rev. Lett. **72**, 1870 (1994). P. Monthoux, D. J. Scalapino, Phys. Rev. Lett. **72**, 1874 (1994).
12. J. Hirsch, Physica B **199–200**, 366 (1994).
13. M. R. Norman, Phys. Rev. Lett. **72**, 2077 (1994).
14. R. Laughlin, Science **242**, 525 (1988). G. Canright, S. M. Girvin, Science **247**, 1197 (1990).
15. D. S. Rokhsar, Phys. Rev. Lett. **70**, 961 (1993).
16. V. L. Berezinskii, JETP Lett. **20**, 287 (1974). A. V. Balatsky, E. Abrahams, Phys. Rev. B **45**, 13125 (1992). A. V. Balatsky, E. Abrahams, J. R. Schrieffer, D. J. Scalapino, to be published in Physica B.
17. V. J. Emery, S. A. Kivelson, Phys. Rev. B **46**, 10812 (1992); Phys. Rev. Lett. **72**, 1918 (1994).
18. P. Coleman, E. Miranda, A. Tsvelik, Phys. Rev. Lett. **70**, 2960 (1993). R. Heid, "On the Thermodynamic Stability of Odd-in-Frequency Superconductivity," preprint, Ohio State U., 1994.
19. P. Nozières, A. Blandin, J. Phys. (Paris) **41**, 193 (1980). A. W. W. Ludwig, I. Affleck, Phys. Rev. Lett. **57**, 3160 (1991).
20. D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987); Physica B **186–188**, 312 (1993). ■