Novel types of superconductivity in f-electron systems

M. Brian Maple

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Compounds of rare earth and actinide elements with partially filled f-electron shells show superconductivity induced by magnetic fields, carried by "heavy" electrons and destroyed below a second critical temperature.

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During the last one and one-half decades, experiments on compounds and alloys of rare earth and actinide elements with partially filled f-electron shells have revealed novel superconducting phenomena. Among these are the reappearance of resistance at a second critical temperature due to the interaction of magnetic moments with conduction electrons, the coexistence of superconductivity and antiferromagnetism, superconductivity induced by magnetic fields and superconductivity due to electrons with large effective masses.

The "f-electron materials" in which these phenomena occur are of two types. In the first type, there are two distinct interpenetrating systems of electrons: a set of localized electrons and a set of itinerant electrons. The localized f electrons carry magnetic moments, while the itinerant electrons are responsible for superconductivity, which is the usual kind involving pairs of electrons—the so-called Cooper pairs—that form under the influence of the attractive electron–phonon interaction and have zero net momentum and spin. The novel superconducting phenomena in the first type of f-electron material arise from the magnetic interaction between the momenta and spins of the conduction electrons and the magnetic moments of the localized f electrons.[1,2]

The second type of f-electron material is characterized by a single band of electrons that is a hybrid of itinerant electrons and localized f electrons. The electrons near the Fermi level have large effective masses, in some instances approaching several hundred times the mass of the free electron, and have been observed[3] to become superconducting, magnetic, both or neither (see PHYSICS TODAY, December 1983, page 20). The observation of superconductivity in these "heavy electron" materials has generated an enormous amount of excitement because the superconductivity was unexpected, has anomalous characteristics and may involve new types or new mechanisms of pairing.

In this article I give a brief overview of the new superconducting phenomena found in compounds and alloys of rare-earth and actinide elements with partially filled f-electron shells. I discuss these phenomena in approximately the order in which they were developed. My focus on the new types of superconductivity means that I do not consider in this article materials containing rare-earth and actinide elements with *empty* or *completely filled* f-electron shells. Such materials are quite conventional superconductors, although some of them have exceptional superconducting characteristics; $LaMo_6Se_8$, for example, has a moderately high superconducting critical temperature of about 11 K and an enormous upper critical magnetic field of about 45 tesla.

Although the research that I describe involves relatively complex materials that exhibit rather esoteric superconducting and magnetic phenomena, it seems reasonable to expect that research (see figure 1) in this exciting field will yield experimental discoveries and theoretical breakthroughs that will be important in future applications of superconductivity to problems in technology. For example, enhancement of the upper critical magnetic field in certain type-II superconductors containing paramagnetic impurities may someday aid in the production of high magnetic fields, while the anomalous superconductivity exhibited by heavy-electron materials may lead to insights that will eventually make it possible to fabricate superconductors with critical temperatures substantially higher than that of Nb_3Ge, which gives us the present upper limit of about 23 K. Of course, we also expect entirely new and surprising developments.

Superconducting Kondo systems

Small concentrations of paramagnetic impurity ions profoundly modify[1] the superconductivity of metals in which they have been dissolved. These modifications include a rapid suppression of the superconducting transition temperature, or critical temperature, as the concentration of the paramagnetic impurities increases, gapless superconductivity and "reentrant" superconductivity, in which superconductivity actually disappears below a certain temperature. The source of these remarkable superconducting phenomena is the exchange interaction between the spins of the conduction electrons and the spins of the impurity ions. Experiments at Bell Laboratories in 1958 first implicated the exchange interaction in unusual superconducting phenomena. In these experiments, Bernd Matthias, Harry Suhl and Er-

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nest Corenzwit found that rare-earth impurities dissolved in the superconductor lanthanum produce strong depressions of the superconducting transition temperature that vary in a nearly linear fashion with the concentration of the rare-earth impurity. The magnitudes of the depressions correlate with the rare-earth ion's spin rather than with its effective magnetic moment.

The exchange interaction between an impurity ion and a conduction electron is described by the Hamiltonian

$$\mathcal{H}_{ex} = -2\mathcal{J}\,\mathbf{S}\cdot\mathbf{s}$$

The coefficient $\mathcal{J}$ characterizes the strength and sign of the interaction, $\mathbf{S}$ is the spin of the impurity ion and $\mathbf{s}$ is the spin density of the conduction electrons at the impurity site. The effect of the exchange interaction is to break up the Cooper pairs, the bound pairs of electrons that form the superconducting condensate. Rewriting the exchange interaction makes this easier to see:

$$\mathcal{H}_{ex} = -\boldsymbol{\mu}\cdot\mathbf{H}_{ex}$$

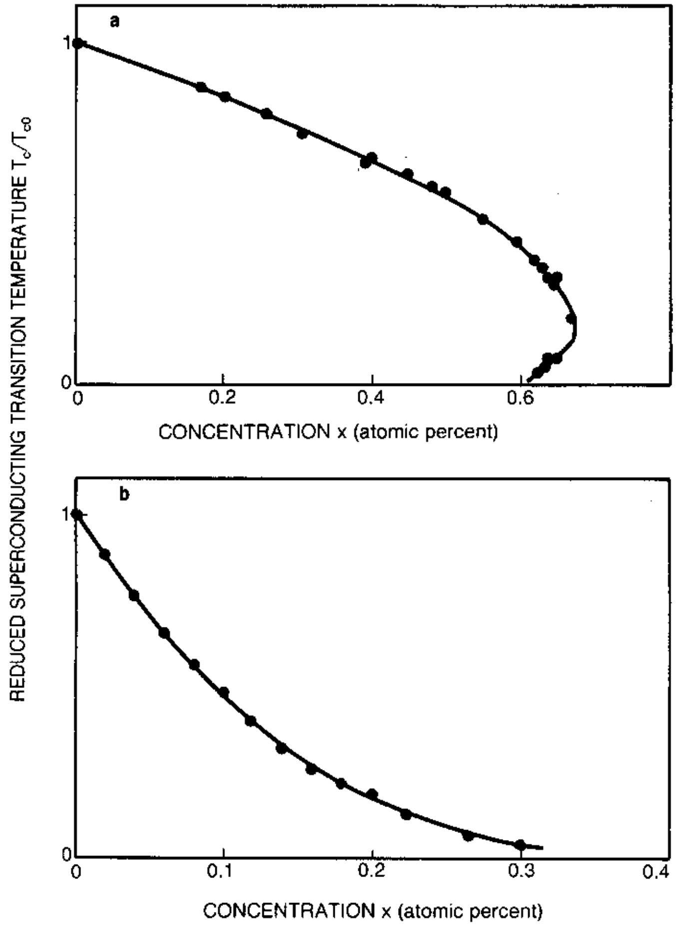
Here $\boldsymbol{\mu}$ is $2\mu_B\mathbf{s}$, the magnetic moment of an electron, and $\mathbf{H}_{ex}$ is $\mathcal{J}\,\mathbf{S}/\mu_B$, a local exchange field that, like a magnetic field, interacts with the magnetic moments (but not the momenta) of the conduction electrons. Because the two electrons in a Cooper pair have opposite momenta and spins, the exchange field $\mathbf{H}_{ex}$ produces a Zeeman-like splitting of the energy levels of the superconducting electrons. The superconducting electron states are thereby broadened in energy by an amount δE, which reduces the energy gap and the lifetime (approximately $\hbar/\delta E$) of the Cooper pairs. Alexei Abrikosov and Lev Gor'kov of the Soviet Union showed theoretically in 1960 that both the superconducting transition temperature and the energy gap are rapidly suppressed as "universal functions" of the relative concentration x of the paramagnetic impurities: The transition temperature goes to zero at a critical concentration x_{cr} and the energy gap vanishes when the impurity concentration x is $0.91x_{cr}$. In the concentration region between $0.91x_{cr}$ and x_{cr}, superconductivity persists without an energy gap. This phenomenon of "gapless superconductivity" aroused the interest and challenged the intuition of many physicists during the 1960s.

The exchange interaction parameter $\mathcal{J}$ has a positive, or Heisenberg, contribution $\mathcal{J}_0$ that depends on the Coulomb exchange integral over the wavefunctions of the conduction electrons and the localized f electrons, as well as a negative contribution $\mathcal{J}_1$ that involves the covalent admixture of conduction-electron and localized f-electron wavefunctions. When the hybridization between the conduction-electron states and localized f-electron states is appreciable, the covalent-mixing contribution exceeds the Heisenberg contribution and the net exchange interaction becomes negative. A negative net exchange interaction favors *antiparallel* alignment of the impurity-ion spins $\mathbf{S}$ and the conduction-electron spins $\mathbf{s}$ and has profound consequences: A many-body singlet ground state forms in which the spins of the paramagnetic impurity atoms and the spins of the conduction electrons are completely correlated, and this gives rise to a set of anomalies in the physical properties. These anomalies are generally known as the Kondo effect.

Dilution refrigerator for cooling f-electron materials to millikelvin temperatures. Here graduate student Jenq-Wei Chen and postdoctoral research physicist Steven Lambert prepare the He^3–He^4 refrigerator for measurements of the upper critical magnetic fields of heavy-electron superconductors. Figure 1

The Kondo effect

The most famous of the Kondo anomalies is a minimum in the electrical



Effect of impurities on superconducting transition temperatures for two systems. **a:** The $La_{1-x}Ce_xAl_2$ system, for which the superconducting transition temperature T_{c0} of the pure host material $LaAl_2$ is 3.30 K and the Kondo temperature is about 0.1 K. **b:** The $Th_{1-x}U_x$ system, for which the transition temperature T_{c0} is 1.36 K and the Kondo temperature is about 100 K. (From reference 1.) Figure 2

resistivity at low temperatures. The minimum is produced by an impurity contribution to the electrical resistivity that increases with decreasing temperature as $-\ln T$ over several decades of temperature. Jun Kondo gave the theoretical explanation for this effect in 1964. He calculated the spin-dependent scattering of conduction electrons by impurity ions to third order in the exchange-interaction parameter $\mathscr{J}$ and showed that the impurity's contribution to the electrical resistivity varies as $-\ln T$ for temperatures greater than the "Kondo temperature" T_K, which is given approximately by $T_F \exp[-1/N(E_F)|\mathscr{J}|]$, where T_F is the Fermi temperature and $N(E_F)$ is the density of states at the Fermi level E_F.

Since Kondo's original work, theorists have struggled to calculate the physical properties of Kondo systems for all values of the temperature ratio T/T_K. A physical interpretation that has emerged from these theories is that the Kondo temperature is a characteristic temperature below which the spins of the impurity ions tend to be compensated by the spins of the conduction electrons, the degree of compensation increasing with decreasing temperature until the impurity is demagnetized at 0 K. This is consistent with the behavior of the contribution χ_i the impurity makes to the magnetic susceptibility; χ_i exhibits localized-magnetic-moment behavior at temperatures much greater than the Kondo temperature and nonmagnetic behavior at temperatures much less than the Kondo temperature. Specifically, for temperatures well above the Kondo temperature, the impurity contribution to the magnetic susceptibility is described by a Curie–Weiss law:

$$\chi_i = N\mu_{eff}^2/3k_B(T-\theta)$$

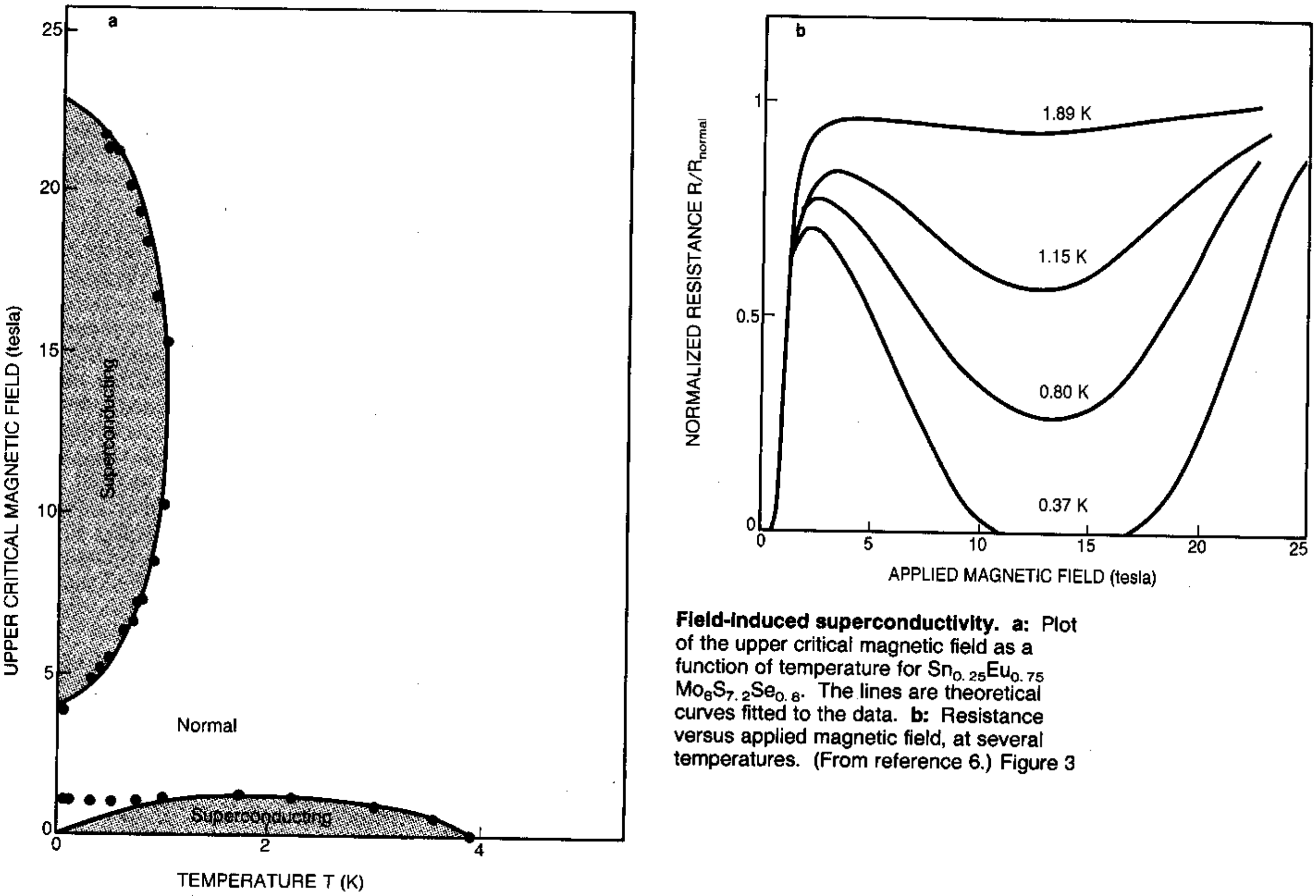
Here N is the number of impurity ions, μ_{eff} is the effective magnetic moment and θ is approximately $-3T_K$; for temperatures well below the Kondo temperature, the impurity contribution to the magnetic susceptibility approaches a constant value as the temperature approaches zero.

Other typical Kondo anomalies include peaks in the heat capacity and thermoelectric power near the Kondo temperature.

In 1974 Kenneth Wilson made one of the major theoretical contributions to the Kondo problem. He used the renormalization-group method to calculate the zero-temperature value of the impurity's contribution to the magnetic susceptibility and to calculate the coefficient γ_i of the impurity's low-temperature contribution $\gamma_i T$ to the specific heat. This was part of the work for which he received the Nobel Prize in 1982. Recently several sophisticated mathematical approaches to the Kondo problem have yielded solutions that are in agreement with experiment for all values of the temperature ratio T/T_K. One can trace the Kondo anomalies to a temperature-dependent resonance in the particle–hole and spin excitation spectra that, at low temperatures, occurs at an energy about $k_B T_K$ above the Fermi level and sets the scale for the low-energy properties.[4]

Reentrant superconductivity. Some of the most unusual and striking manifestations of the Kondo effect occur in the superconducting state and are produced by the competition between singlet spin pairing of conduction electrons in the superconducting state and antiparallel alignment of conduction-electron spins with impurity spins in the so-called Kondo quasi-bound state. Because the relevant energy of the superconducting state is of order $k_B T_{c0}$, where T_{c0} is the transition temperature of the superconducting host material without impurities, and because the characteristic energy of the quasi-bound state is of order $k_B T_K$, the largest effects are expected, and indeed are observed, in systems in which the Kondo temperature is about the same as the transition temperature T_{c0}.

The phenomenon of reentrant superconductivity due to the Kondo effect was first observed in the early 1970s at the University of Cologne and the University of California, San Diego, in the system $La_{1-x}Ce_xAl_2$, consisting of the superconducting compound $LaAl_2$ with paramagnetic Ce impurities replacing some of the La atoms. The superconducting transition temperature T_{c0} of the $LaAl_2$ host compound is 3.3 K and the Kondo temperature is about 0.1 K. Figure 2a shows data for the superconducting transition temperature T_c as a function of the Ce



Field-induced superconductivity. a: Plot of the upper critical magnetic field as a function of temperature for $Sn_{0.25}Eu_{0.75}Mo_6S_{7.2}Se_{0.8}$. The lines are theoretical curves fitted to the data. **b:** Resistance versus applied magnetic field, at several temperatures. (From reference 6.) Figure 3

impurity concentration x in units of atomic percent for the $La_{1-x}Ce_xAl_2$ system. Alloys with Ce concentrations within the range 0.6–0.7 atomic percent exhibit two transition temperatures, denoted T_{c1} and T_{c2}; as such an alloy is cooled to low temperatures, it becomes superconducting at T_{c1} and returns at T_{c2} to the normal state, where it remains down to at least 6 mK, the low-temperature limit of the experiments.

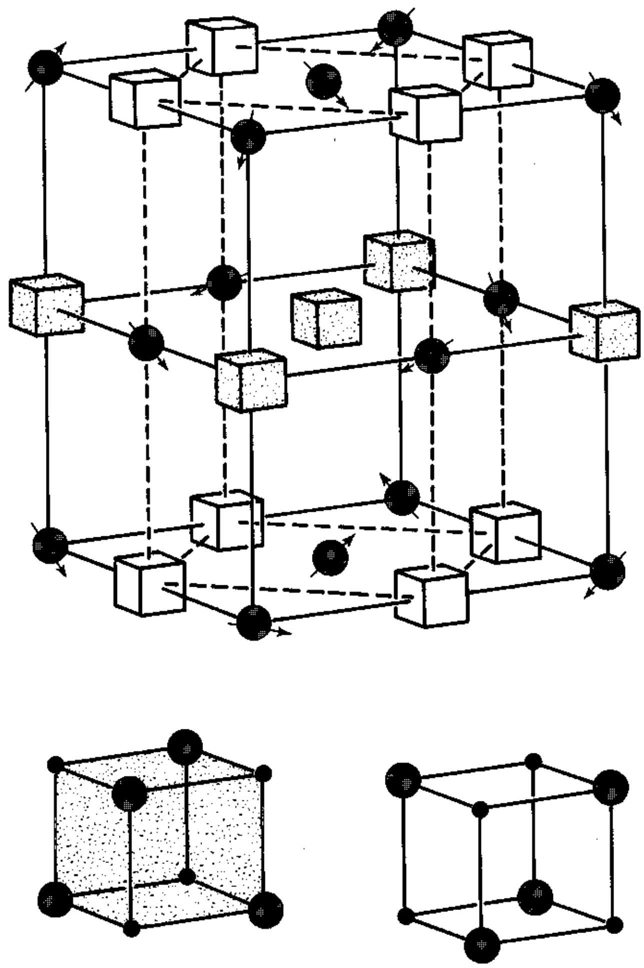
In the early 1970s, Erwin Muller-Hartmann and Hans Zittartz of the University of Cologne, in West Germany, carried out some of the earliest calculations of transition temperature as a function of impurity concentration for superconducting Kondo systems. Their calculations indicated[5] reentrant superconductive behavior when T_K is far below T_{c0}. In the opposite limit, T_K far above T_{c0}, the calculations of the Cologne group and others predicted nearly exponential dependences of transition temperature on impurity concentration. An example of a system with such a dependence is $Th_{1-x}U_x$, for which the transition temperature T_{c0} is 1.4 K and the Kondo temperature T_K is about 100 K (figure 2b).

Compensation effect

Besides producing the Kondo effect, a negative exchange interaction between conduction-electron spins and impurity spins can produce other interesting superconducting phenomena. These include enhancement of the upper critical magnetic field H_{c2} and superconductivity induced by magnetic fields in type-II superconductors containing paramagnetic ions. The mechanism responsible for both phenomena is the compensation by an applied magnetic field of the exchange field associated with the paramagnetic impurity ions. This compensation effect, which I describe below, was proposed more than 20 years ago at Bell Labs by Vincent Jaccarino, now at the University of California, Santa Barbara, and Martin Peter, now at the University of Geneva.

An applied magnetic field is expelled from the interior of a type-I superconductor, a phenomenon that is known as the Meissner effect. In contrast, an applied field can penetrate into the interior of a type-II superconductor provided it is between the lower critical field H_{c1}, below which it is expelled, and the upper critical field H_{c2}, above which the superconductivity is destroyed. In a type-II superconductor, the London penetration depth—the distance over which the supercurrents screen away a magnetic field—exceeds the coherence length, the distance over which the superconducting order parameter deviates from its equilibrium value. As a result it is energetically favorable for the magnetic field to penetrate into the interior of the superconductor as thin filaments of flux consisting of a normal core of radius about equal to the coherence length, where the magnetic field is high, surrounded by a vortex of supercurrent that screens the magnetic field to zero exponentially over a characteristic distance about equal to the London penetration depth. Each filament of flux contains one flux quantum Φ_0, of magnitude $hc/2e$, and the filaments form a triangular lattice.

The exchange field compensation effect involves an intricate interplay among the upper critical, exchange and applied magnetic fields of type-II superconductors that contain impurity ions with spins coupled to the spins of the conduction electrons via a negative exchange interaction. This effect is best described by considering the two mechanisms that determine the upper critical field H_{c2} of a type-II superconductor. The first of these is the interaction of the momenta of the conduction electrons with the magnetic field: $(e/mc)(\mathbf{p}\cdot\mathbf{A})$, where $\mathbf{A}$ is the magnetic vector potential. This interaction gives rise to the orbital critical field $H_{c2}{}^*$. The second mechanism is the Zeeman interaction of the magnetic field and the magnetic moments (or spins) of the conduction electrons: $-\boldsymbol{\mu}\cdot\mathbf{H} = -2\mu_B(\mathbf{s}\cdot\mathbf{H})$. This interaction produces the Pauli paramagnetic limiting field



Crystal structure of tetragonal rare earth rhodium borides, RRh_4B_4. The dashed outline shows the unit cell. Green circles represent rare earth atoms; the randomly oriented arrows indicate magnetic moments in the disordered, or paramagnetic, state. Orange and blue represent rhodium and boron, respectively. The Rh_4B_4 clusters, shown in detail at the bottom of the figure, are not drawn to scale. (From reference 2.) Figure 4

H_P. The resultant upper critical field H_{c2} is always lower than the smaller of $H_{c2}^*(T)$ and $H_P(T)$.

The situation becomes more involved when localized magnetic moments are present, because alignment of the moments by an applied magnetic field can produce a net polarization that acts on the conduction-electron spins via the exchange interaction. The net exchange field is given by

$$\mathbf{H}_{ex} = \sum_i (\mathscr{J}/\mu_B)\mathbf{S}_i = x(\mathscr{J}/\mu_B)\langle S_z\rangle \quad (1)$$

Here x is the concentration of paramagnetic ions and $\langle S_Z\rangle$ is the average value of the component of the spin $\mathbf{S}$ in the direction of the applied field $\mathbf{H}$. Thus the total magnetic field acting on the spins of the conduction electrons is equal to the sum of the applied magnetic field $\mathbf{H}$ and the exchange field $\mathbf{H}_{ex}$:

$$\mathbf{H}_T = \mathbf{H} + \mathbf{H}_{ex} = \mathbf{H} - x(|\mathscr{J}|/\mu_B)\langle \mathbf{S}_z\rangle$$

The magnitude of the spin component $\langle S_Z\rangle$ increases with the applied magnetic field $\mathbf{H}$ because the spins tend to align with the field, and decreases with the temperature because thermal fluctuations tend to randomize the orientations of the spins. For certain applied fields and temperatures, the exchange field $H_{ex}(H,T)$ can actually be compensated by the applied field so that H_T, the sum of the applied and exchange fields, is zero.

Field-induced superconductivity. On the boundary between the superconducting and normal states, that is, at the upper critical magnetic field $H_{c2}(T)$, the applied magnetic field H completely penetrates into the interior of the superconducting material. When the upper critical field H_{c2} is determined by the Pauli paramagnetic limiting field H_P, the system remains superconducting as long as the magnitude of the net field H_T does not exceed H_P. If the magnitude of the exchange field H_{ex} is less than the Pauli paramagnetic limiting field H_P for all temperatures and applied fields H, then superconductivity will occur for $0 \leqslant H \leqslant |H_{ex}| + H_P$, leading to an enhancement of the upper critical field H_{c2} above the Pauli field H_P by an amount $|H_{ex}|$. Because $|H_{ex}|$ increases with increasing applied field H and decreasing temperature T, the $H_{c2}(T)$ curve will develop positive curvature. Enhanced $H_{c2}(T)$ curves with positive curvature have been observed in $M_{1-x}Eu_xMo_6S_8$ systems, with M representing Sn, Pb, La and Yb, as well as $EuMo_6S_8$ under pressure.

On the other hand, if the magnitude of the exchange field exceeds the Pauli field for certain temperatures and applied fields, then there are two domains of superconductivity, one at low applied fields H (between 0 and $|H_{ex}| - H_P$) and another at high applied fields (between $|H_{ex}| - H_P$ and $|H_{ex}| + H_P$). Researchers at the University of Geneva recently established[6] two domains of superconductivity in the H–T plane for the system $Sn_{0.25}Eu_{0.75}Mo_6S_{7.2}Se_{0.8}$, as figure 3 illustrates. The solid lines in the figure are boundaries of the two superconducting domains obtained from calculations, the parameters of which have been adjusted to give the best fit to the data. Because the upper critical field H_{c2} is also limited by the orbital critical field H_{c2}^*, the latter field must be large enough to allow superconductivity to occur in the high-field domain: $H_{c2}^* > |H_{ex}| - H_P$.

While magnetic-field-induced superconductivity appears to have been verified for a paramagnetic system, it has not yet been established for a ferromagnet as originally proposed by Jaccarino and Peter. Magnetoresistance data on the compound $CePb_3$, which appears to exhibit antiferromagnetic order below 1.1 K, have recently been interpreted[7] in terms of magnetic-field-induced superconductivity, although this result remains to be confirmed by specific-heat measurements.

Superconductivity and magnetism

The subject of the interplay between superconductivity and magnetism is now nearly three decades old. Vitaly Ginzburg of the Soviet Union made the first theoretical inquiry into this topic in 1957, and experimental investigations by Matthias, Suhl and Corenzwit followed in 1959. Although there was significant progress on this problem during the 1960s, especially in the theory, the most important developments occurred after about 1976, when investigators found[2] that certain ternary compounds consisting of a rare earth element and two other elements exhibit long-range magnetic order in the superconducting state.

Ternary rare earth systems. The series of isostructural ternary rare earth compounds that have been investigated most extensively in connection with the interaction between superconductivity and long-range magnetic order include the rhombohedral rare earth (R) molybdenum chalcogenides RMo_6S_8 and RMo_6Se_8 and the tetragonal rare earth rhodium borides RRh_4B_4. The building blocks of these ternary rare earth phases are rare earth ions and the molecular units, or "clusters," Mo_6S_8, Mo_6Se_8 and Rh_4B_4. Figure 4 is a schematic representation[2] of the crystal structure of the RRh_4B_4 compounds. The superconductivity is believed to be associated primarily with the transition-metal d electrons, which are more or less confined within the clusters, while the long-range magnetic order involves the localized 4f electrons of the rare earth ions, which occupy an ordered sublattice. The rather weak exchange interaction between the conduction electrons and the rare earth ions accounts for the persistence of superconductivity even in the presence of relatively large concentrations of rare earth ions. The exchange interaction also produces long-range magnetic ordering via the "RKKY" mechanism, which is an indirect interaction between rare earth magnetic moments that is mediated by the conduction electrons through the exchange interaction, although the direct magnetic interaction between the rare earth magnetic moments may be important in certain cases.

Antiferromagnetic superconductors. The first observations[2] of the coexistence of superconductivity and long-range antiferromagnetic order were made independently on certain RMo_6S_8 compounds at the University of Geneva and on various RMo_6Se_8 and RRh_4B_4 compounds at the University of California, San Diego. The simplest antiferromagnetic structure consists of two interpenetrating *ferromagnetic* sublattices whose magnetic moments, which are parallel within each sublattice, are oriented in opposite directions. In retrospect, superconductivity in such a material is not surprising, because over the scale of a superconducting coherence length—several hundred angstroms or more—the exchange and internal magnetic fields of an antiferromagnet alternate in direction many times and average to zero. However, antiferromagnetic order can affect superconductivity by means of a variety of mechanisms, producing anomalies in physical properties in the vicinity of the Néel temperature, the temperature below which the antiferromagnetic order occurs. This is illustrated in figure 5, which shows plots of the upper critical magnetic field H_{c2} as a function of temperature for polycrystalline samples of the nonmagnetic superconductor $LuRh_4B_4$, the antiferromagnetic superconductors $NdRh_4B_4$ and $SmRh_4B_4$ and the ferromagnetic superconductor $ErRh_4B_4$. The antiferromagnetic superconductors $NdRh_4B_4$ and $SmRh_4B_4$ show both enhancements and depressions of this critical field below their Néel temperatures; $NdRh_4B_4$ has two antiferromagnetic phases. The lack of universal behavior is due to the large number of mechanisms through which antiferromagnetic order modifies superconductivity.[2]

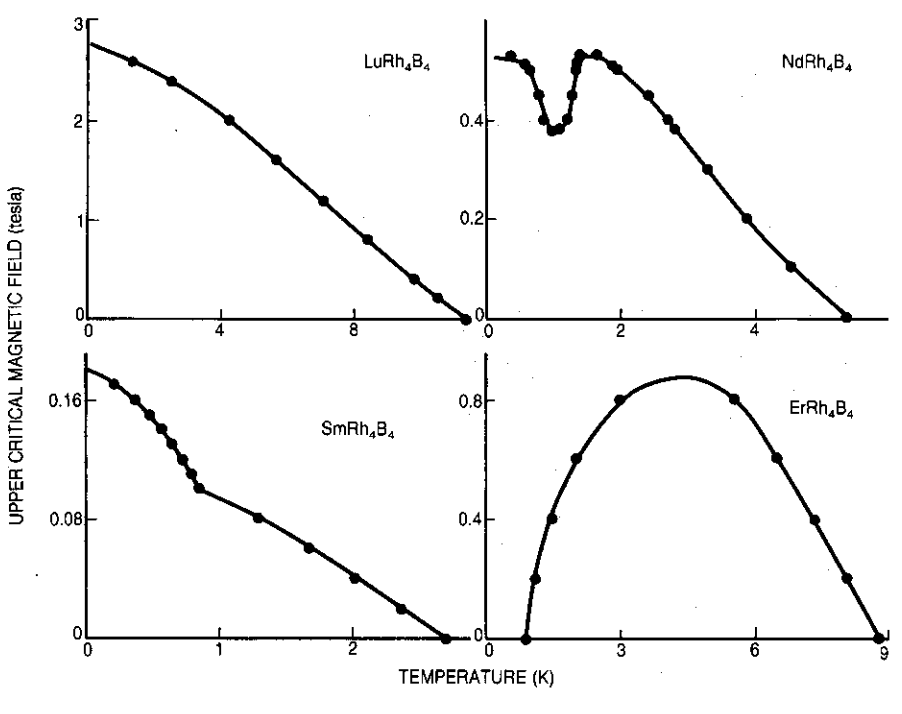
Reentrance due to ferromagnetism. Several ternary rare earth compounds exhibit reentrant superconductivity due to the onset of long-range ferromagnetic order. Extensive investigations on two of these materials, $HoMo_6S_8$ and $ErRh_4B_4$, reveal a second-order superconducting transition at an upper critical temperature T_{c1} and a first-order transition back to the normal state at a lower critical temperature T_{c2}, which is about equal to the Curie temperature T_M, the temperature below which the ferromagnetism occurs. Figure 5 shows the H_{c2} vs T curve for a polycrystalline specimen of $ErRh_4B_4$.

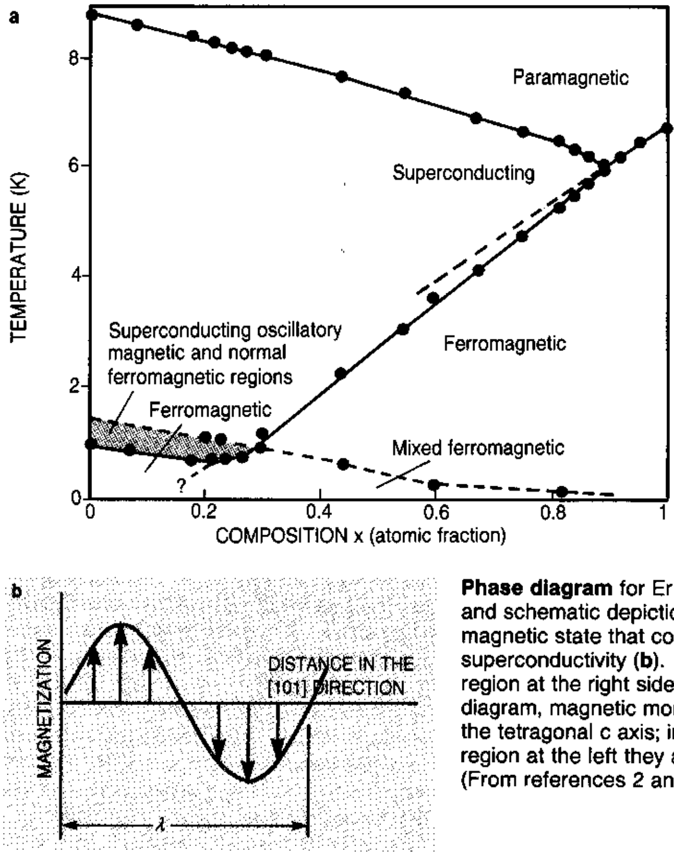
Ferromagnetism occurs at the expense of superconductivity because the decrease in free energy relative to the paramagnetic normal state is much larger for ferromagnetism than for superconductivity. This reflects the fact that the number of magnetic ions, xN, is much larger than the number of conduction electrons, which is about $(k_B T_{c1}/E_F)N$; here N is the total number of atoms and x is the atomic fraction of magnetic ions, each of which contributes an energy of about $k_B T_M$ to the magnetic free energy. Each conduction electron supplies an energy of about $k_B T_{c1}$ to the superconducting free energy. Reentrant superconductivity due to the onset of ferromagnetic order was predicted by Gor'kov and Anatole Rusinov of the Soviet Union in 1962.

Oscillatory magnetic state

The interaction between superconductivity and ferromagnetism leads to some rather remarkable phenomena in the vicinity of the lower critical temperature T_{c2} in reentrant ferromagnetic superconductors. Small-angle neutron scattering experiments on both $HoMo_6S_8$ and $ErRh_4B_4$ have revealed the existence of an oscillatory magnetic state that coexists with superconductivity in a narrow temperature interval above the temperature T_{c2}. In the oscillatory magnetic state, the magnetization of the rare earth ions has a sinusoidal dependence on distance with a wavelength λ of a few hundred angstroms. Moreover, the regions within which superconductivity and the oscillatory magnetic state coexist appear to be interspersed with normal ferromagnetic domains, resulting in a spatially inhomogeneous state. Neutron diffraction measurements on a single-crystal specimen of $ErRh_4B_4$ have revealed[8] that the oscillatory magnetic state in this compound is a transverse linearly polarized long-range magnetic structure with a wavelength λ of about 100 Å in which the

Upper critical magnetic field as a function of temperature for polycrystalline samples of various materials. The superconductor $NdRh_4B_4$ has two antiferromagnetic phases, with Néel temperatures of 0.9 K and 1.3 K. The compound $SmRh_4B_4$ has a Néel temperature of 0.87 K, while $ErRh_4B_4$ shows ferromagnetic ordering at about 1 K. (From reference 2.) Figure 5





Phase diagram for $Er_{1-x}Ho_xRh_4B_4$ **(a)** and schematic depiction of the oscillatory magnetic state that coexists with superconductivity **(b)**. In the ferromagnetic region at the right side of the phase diagram, magnetic moments are parallel to the tetragonal c axis; in the ferromagnetic region at the left they are perpendicular. (From references 2 and 9.) Figure 6

magnetization lies along the [010] axis and the wavevector is in the [101] direction (see figure 6b).

The oscillatory magnetic state that coexists with superconductivity in $HoMo_6S_8$ and $ErRh_4B_4$ is reminiscent of the "cryptoferromagnetic state" that Philip Anderson and Suhl proposed in 1959 when they were at Bell Laboratories, and that has been the object of much theoretical interest in recent years. Whereas Anderson's and Suhl's original theory is based on the exchange interaction between the spins of the rare earth ions and the spins of the conduction electrons, more recent theories involve the electromagnetic interaction between the magnetic moments of the rare earth ions and the momenta of the conduction electrons. These theories have been proposed independently by several research groups, including Eugene Blount and Chandra Varma of Bell Laboratories and Hideki Matsumoto and Hiroomi Umezawa of the University of Alberta, Canada, working in collaboration with Masashi Tachiki of Tohoku University, Sendai, Japan. In these models, the interaction between the rare earth magnetic moments at long wavelengths is screened by the persistent current, leading to an oscillatory magnetic state with a wavelength given by

$$\lambda \sim (\lambda_L \xi_M)^{1/2} \qquad (2)$$

In this approximation λ_L is the London penetration depth and ξ_M is a length parameter characterizing the "stiffness" of the coupling between the magnetic moments of the rare earth ions: The larger the parameter ξ_M, the stronger is the coupling between the spins. Physically, the oscillatory magnetic state comes about in the following way: If a spontaneous magnetization develops within a superconductor, the supercurrents will screen the magnetization away over a distance on the order of the London penetration depth λ_L; this is the Meissner effect. However, the screening process will be accompanied by an increase in the kinetic energy of the conduction electrons. The increase in the kinetic energy can be reduced if the magnetization develops a modulation with a wavelength comparable to the penetration depth λ_L, although at the expense of an increase in magnetic energy. A reasonable compromise between the increases in the kinetic and magnetic energies is achieved for the wavelength given by equation 2.

Experiments on mixed ternary rare earth compounds are another method for studying the interaction between superconductivity and long-range magnetic order, as well as for exploring the effects of competing types of magnetic-moment anisotropy or magnetic order. Investigators have studied a number of mixed ternary systems formed by substituting various rare earth elements at the rare earth sites or by substituting various transition-metal elements at the transition-metal sites. One of the more interesting systems is $Er_{1-x}Ho_xRh_4B_4$, whose low-temperature phase diagram,[2,9] delineating the paramagnetic, superconducting and magnetically ordered phases, appears in figure 6a.

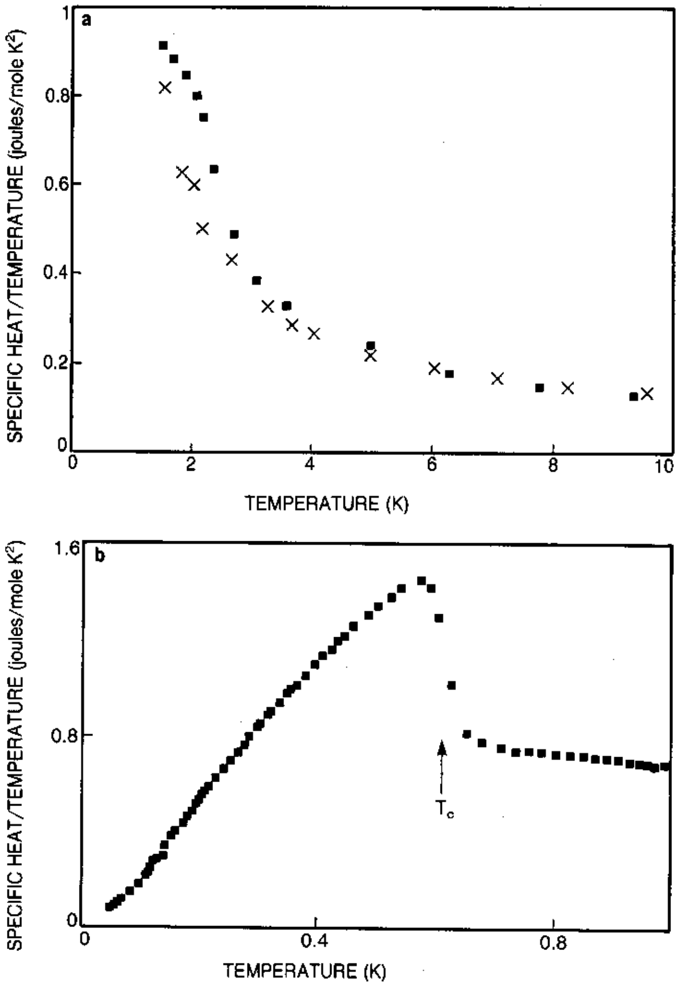
Heavy-electron superconductors

Recently there has been a great deal of interest[3] in the small but growing class of heavy-electron superconductors. These new superconductors belong to a larger group of heavy-electron materials—frequently referred to as heavy-fermion materials—that consist of rare earth and actinide compounds that have electrons with effective masses as high as several hundred times the mass of the free electron and ground states that are superconducting, magnetic, both or neither. Thus far, experimenters have observed heavy-electron superconductivity in such compounds as $CeCu_2Si_2$, UBe_{13}, UPt_3, U_2PtC_2, URu_2Si_2 and U_6Fe, listed here in order of decreasing effective electron mass. The unusual superconducting properties[10–12] of the compounds with the largest effective masses—$CeCu_2Si_2$, UBe_{13} and UPt_3—has led to speculation that these materials may be displaying an unconventional type of superconductivity.

Origin of the heavy electrons. The effective masses of the heavy-electron materials are inferred from the coefficients γ of the electronic contribution γT to their low-temperature specific heat. In the heavy-electron materials, the coefficients γ attain values up to several J/mol K^2, a thousand times larger than the mJ/mol K^2 values for typical metals. Moreover, the coefficients γ are often found to decrease by as much as an order of magnitude as the temperature is increased from about 0 K to about 10 K, in contrast to the situation for typical metals, for which the coefficients are constant. The data in figure 7 illustrate the large magnitude and characteristic temperature dependence[3] of the coefficients γ for the heavy-electron compounds $CeCu_2Si_2$ and UBe_{13}. In the 0–10 K temperature range, the coefficient γ is the ratio of the specific heat to the temperature because the lattice contribution to the specific heat, which has the form $C_l = \beta T^3$, is negligible compared with the electron contribution.

For a gas of free electrons, which is the simplest approximation one can make to a metal, the specific heat coefficient γ is proportional to the density of electron states $N(E_F)$ at the Fermi level, which in turn is proportional to the mass of the electrons and inversely proportional to the Fermi temperature T_F. The Fermi temperature, or degeneracy temperature, determines the fraction of electrons near the

Specific heat divided by temperature, plotted as a function of temperature for $CeCu_2Si_2$ (squares in **a** and **b**) and UBe_{13} (crosses in **a**) in their normal, or nonsuperconducting, states.[3] The plot in **b** shows the specific-heat anomaly associated[12] with the superconducting transition of $CeCu_2Si_2$ at about 0.6 K. Figure 7



Fermi level that are nondegenerate; that fraction is given approximately by the temperature ratio T/T_F. In a degenerate free-electron gas, each of the plane-wave states specified by a wavevector is occupied by two electrons, one with spin up and the other with spin down, up to the Fermi level. Thus the Fermi temperature T_F represents a characteristic temperature over which the physical properties of the electron gas evolve from low-temperature (T far below T_F) quantum behavior, or Fermi–Dirac behavior, to high-temperature (T far above T_F) classical behavior, or Maxwell–Boltzmann behavior. Specifically, when the temperature becomes comparable to the Fermi temperature, both the specific-heat coefficient γ and the Pauli magnetic susceptibility χ_P, which are temperature independent at temperatures well below the Fermi temperature, become temperature dependent and decrease with increasing temperature. However, this behavior is not observed in typical metals, because their Fermi temperatures are on the order of 10^4 K.

In a more realistic model of a metal in which the electrons are allowed to interact with one another, the coefficient γ has the same form as for a free-electron gas, but with the electron mass m and the Fermi temperature T_F replaced by an effective mass m^* and effective Fermi temperature T_F^*. In the heavy-electron materials, one can interpret the large values of the specific-heat coefficient in terms of the large effective electron masses, or, equivalently, the small effective Fermi temperatures, which are on the order of several kelvins or several tens of kelvins. Such small effective Fermi temperatures set the scale for the temperature dependence of the specific-heat coefficient γ and are consistent with the data shown in figure 7 for the superconductors $CeCu_2Si_2$ and UBe_{13}.

The small effective Fermi temperatures or large effective electron masses in the heavy-electron materials suggest that there is a large, narrow peak, or resonance, in the density of states $N(E_F)$ near the Fermi level E_F. Electrons in such a large narrow peak at the Fermi level will dominate the physical properties and become nondegenerate when the temperature becomes comparable to the effective Fermi temperature, which is given by E_F^*/k_B. The numerator E_F^* is the effective Fermi energy, which is the difference $E_F - E_b$, where E_b is the lowest energy of electrons in the narrow peak. The most obvious source of a narrow feature in the density of states near the Fermi level is the electron band structure produced by Bragg scattering of electron waves from crystal planes. However, band-structure calculations on several heavy-electron materials yield enhanced values of the density of states that fall far short of those inferred from the measured values of the specific-heat coefficient γ, suggesting[11] that many-body interactions among the electrons are responsible for the heavy-electron phenomena.

Another source of a narrow feature in the density of states near the Fermi level emerges from valence-fluctuation or Kondo-lattice models, both of which involve the hybridization of f-electron and conduction-electron states. Physicists originally developed these models to describe the anomalous physical properties of certain compounds of the rare earth elements Ce, Sm, Eu, Tm and Yb. In valence-fluctuation models the narrow feature in the density of states is associated with two degenerate hybridized f-electron states that differ in electron occupation by unity and are tied to the Fermi level, whereas in Kondo-lattice models the narrow feature presumably arises from a lattice analog of the Kondo resonance discussed earlier. We do not yet have a completely satisfactory theoretical description of either of these models, but it is generally believed[11] that the underlying concepts will eventually be capable of accounting for the remarkable physical properties of the unusual f-electron materials of which the heavy-electron systems make up a subset.

In the heavy-electron materials, the large, temperature-dependent γ coefficients are accompanied by characteristic anomalies in other physical properties such as the magnetic susceptibility, electrical resistivity and thermoelectric power and in phenomena such as the Hall effect. The anomalies in the magnetic susceptibility and electrical resistivity are especially revealing. Above a characteristic temperature the behaviors of the magnetic susceptibility and electrical resistivity are consistent with the presence of *localized* 4f or 5f electrons, which carry magnetic moments: The temperature dependence of the magnetic susceptibility can be described by a Curie–Weiss law such as equation 1 with the effective magnetic moment close to the value expected from Hund's rules for determining the ground states of atoms; the electrical resistivity has a large value on the order of 10^2 $\mu\Omega$ cm, indicative of strong charge or spin-disorder scattering. However, as the temperature decreases through the characteristic temperature toward 0 K, the behaviors of the magnetic susceptibility and electrical resistivity become reminiscent of that which characterizes *delocalized* 4f or 5f electrons: The susceptibility tends to saturate to a constant value as the temperature T approaches 0 K and the resistivity decreases rapidly and often exhibits a T^2 dependence, a characteristic behavior of Fermi liquids.

Unconventional superconductivity?

It is remarkable that any of the heavy-electron materials exhibit superconductivity in view of the narrow f-electron resonance near the Fermi level. As figure 2b reveals, the substitution of only about 0.3 atomic percent of uranium destroys the superconductivity of thorium, either through pair breaking associated with the Kondo effect or pair weakening via strong Coulomb repulsion between electrons that scatter into the narrow uranium resonances. Nevertheless several heavy-electron materials exhibit bulk superconductivity in the vicinity of 1 K. The superconductivity involves the same heavy-fermion quasiparticles that are responsible for the enormous specific-heat coefficients γ, as evidenced by the jump in the specific heat associated with the second-order transition into the superconducting state. The magnitude ΔC of this jump is comparable to the value $1.43\gamma T_c$ predicted by BCS theory. Figure 7b illustrates[12] this for $CeCu_2Si_2$; here the jump ΔC is approximately γT_c.

Although the transition temperatures of the heavy-electron superconductors are all relatively small, the upper critical magnetic fields and their initial slopes, $-dH_{c2}/dT$ evaluated at T_c, can be enormous. For example, plots of the upper critical magnetic field as a function of temperature for UBe_{13} reveal an anomalous temperature dependence of that critical field and an initial slope of 42 tesla/K, larger than for any other known three-dimensional superconductor, including the high-temperature, high-field A15 and Chevrel-phase superconductors.[13]

At temperatures well below the transition temperature, the superconducting properties of many of the heavy-electron superconductors appear to have power-law temperature dependences, varying as T^n, where n is an integer, rather than exponential temperature dependences $\exp(-\Delta/k_B T)$, where Δ is the energy gap, expected for a conventional BCS superconductor. These properties include the specific heat, thermal conductivity, ultrasonic attenuation and nuclear-spin–lattice relaxation rate.[14] The power-law temperature dependences have been interpreted as evidence for anisotropic superconductivity, in which the energy gap vanishes at points or lines on the Fermi surface. In a conventional BCS superconductor, the energy gap is isotropic, or only weakly varying over the Fermi surface.

The existence and anomalous properties of superconductivity in heavy-electron systems suggest that this superconductivity may be unconventional. One intriguing possibility is that the type of superconductivity displayed by these systems is similar to the triplet superfluidity found in liquid helium-3. A strongly interacting Fermi liquid with a large effective mass and an enhanced Pauli susceptibility, liquid helium-3 undergoes a transition into two superfluid phases below about 3 mK. Repulsive He–He interactions induce the formation of helium-3 "quasiparticle" pairs in spin "triplet" and spatial "p-wave" states in which the helium-3 nuclear spins are aligned parallel to one another and the orbital angular momentum is unity. In fact, the A phase of superfluid helium-3 corresponds to a triplet state called the axial state, in which the energy gap vanishes at the north and south poles of the Fermi surface. Thus, in analogy with helium-3, something akin to triplet spin pairing of electrons under the influence of the repulsive Coulomb interaction may be involved in heavy-electron superconductivity. It is well known that the Coulomb interaction between electrons favors parallel alignment of spins, the most notable example being ferromagnetism. The dominant interaction between electrons in a conventional BCS superconductor is mediated by lattice vibrations, or phonons, and favors the formation of spin "singlet" and spatial "s-wave" pair states in which the electron spins are aligned antiparallel to one another and the orbital angular momentum is zero. However, the strong spin–orbit interaction and crystalline nature of the heavy f-electron systems require that the superconducting state be classified as having odd or even parity, rather than singlet or triplet character, due to the absence of rotational symmetry in spin space.

Additional effort is clearly needed to determine the origin of the exotic superconducting state in heavy-electron materials, and work on this problem is proceeding at a rapid pace. It will be interesting to see whether heavy-electron superconductivity is actually the counterpart of liquid helium-3's triplet superfluidity or a variant of conventional BCS singlet superconductivity due to unusual electron and lattice interactions in heavy-electron systems—or a type of superconductivity involving an altogether new and unexpected kind or mechanism of pairing. An important part of this endeavor will be the investigation of the alternative charge-ordered and spin-ordered ground states found in some of the heavy-electron materials.

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