Heavy Fermion Superconductivity

Charles M. Steiner

Phys. 569, December 25, 2011

Historical background

Heavy fermion materials are a class of compounds named for the enormous effective mass of their charge carriers. This is achieved by a sharp spike in the density of states at the Fermi surface, to as much as 1000 times the density of states in copper (Coleman, 2007). Heavy fermions were discovered in $CeAl_3$ by Andres, Graebner and Ott in 1975, which showed anomalously large heat capacity and magnetic susceptibility.

Much of the theoretical picture was already in place at the time of the discovery of heavy-fermion materials, though they took a few years to be connected. In 1961, Anderson had formulated a theory of magnetic moments in metals, including on-site interactions and a coupling between localized spins and the free electron density. This led to an antiferromagnetic coupling between the local moments and the free electrons. Kondo, in 1962, went beyond the lowest-order approximation to determine the scattering rate from such a screened magnetic impurity. He found that the scattering rate contained a term proportional to the log of T^{-1}. When added to the phonon scattering rate, this effect leads to a low-temperature minimum in the resistance of metals with magnetic impurities. This resistance minimum had been observed as early as the 1930s, but was not definitively linked to magnetic impurities until Clogston et al., 1962.

Doniach, in 1977, first proposed how heavy fermion metals could be the result of a dense lattice of magnetic moments screened by conduction electrons - called a Kondo lattice. Like for isolated impurities, the scattering off of screened magnetic moments can lead to increased resistance at low temperatures. But at even lower temperatures, the charge carriers get into eigenstates of the lattice - the scattering from each lattice site becomes in phase with the others, and resistance drops dramatically.

Superconductivity in heavy-fermion materials was discovered almost simultaneously with the materials themselves. Bucher et al. in 1975 measured superconductivity in UBe_{13}, but dismissed it as an artifact because magnetic moments break up BCS superconductivity, which at the time seemed like the only model. The following year, however, Steglich et al. discovered superconductivity more convincingly in $CeCu_2Si_2$ (Steglich et al., 1976). This opened up the door to non-BCS superconductivity.

In the decade following, there was quick experimental and theoretical progress. In experiment, de Haas-van Alphen measurements were important in solidifying the heavy fermion model. UBe_{13} was confirmed as a superconductor, as were several other heavy fermion materials. Measurements of the magnetic properties and specific heat demonstrated that the heavy fermions were the superconducting charge carriers. Specific heat, NMR, and ultrasonic attenuation experiments were also all consistent with anisotropic energy gaps, containing lines where the gap went to 0.

Theoretical work on heavy fermion materials increased in pace in 1981, when Anderson introduced the large-degeneracy expansion as a tool to calculate the properties of the Kondo lattice model. Although it seems odd to use perturbation theory about infinite degeneracy when some heavy fermion materials have a magnetic degeneracy of 2, this approach allowed roughly correct calculations of spectra and band structure.

Around the same time, several possible mechanisms were being explored for heavy fermion superconductivity, notably the spin fluctuation mechanism, published in 1986 by Monod et al. among others. Something else also happened in 1986: superconductivity was discovered in the cuprates. Because of this first mover advantage, ideas and procedures that originated in the study of heavy fermion superconductors have had a large impact on the study of all future unconventional superconductors.

In the nineties, a lot of interesting work explored the phase diagrams of heavy fermion superconductors. When tuned with doping, pressure, or magnetic field, many heavy fermion materials have quantum critical points - two phases that only touch at zero temperature, separated by a "quantum critical" region at positive temperature. In the quantum critical region, quantum fluctuations dominate the classical thermodynamic ones. Several heavy fermion superconductors have been discovered by looking for superconductivity in the vicinity of these quantum critical points, suggesting that they are closely related.

The Kondo lattice model

In order to understand heavy fermion superconductors, the Kondo lattice model is a good starting point, and this starts with the work of Anderson in 1961. In order to understand the behavior of magnetic impurities in metals, the Anderson Hamiltonian describes the coupling of electrons in the outer orbital of the magnetic impurity to the conduction electrons of the metal.

The Anderson Hamiltonian comes in three parts. The first part is simply the kinetic energy of the conduction electrons. The second part is the Hamiltonian of electrons on the atom - both a binding energy and an on-site repulsion. The third part is a magnetic interaction term between the electrons on the atom and the conduction electrons. Left to themselves, the atoms will form a magnetic ground state. But with the introduction of the interaction term, that's no longer an energy eigenstate - the atom slowly exchanges spins with the surrounding conduction electrons (Anderson, 1961).

At low energies, related to the frequency ω of this spin exchange, there is a resonance which leads to an increase in the scattering cross-section, and thus an increase in the resistance (Kondo, 1962). The Kondo temperature T_K is the characteristic temperature at which this effect becomes large, determined by $k_B T_K = \hbar\omega$.

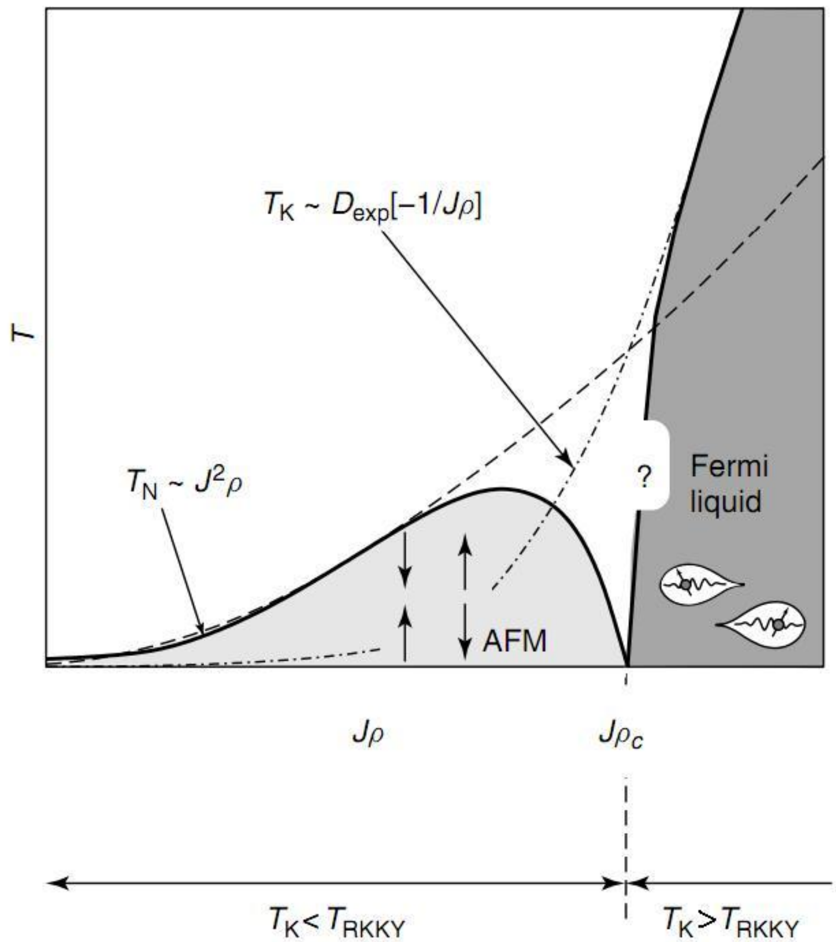


Fig. 1

Diagram of T_K and T_{RKKY} (T_N). When $T_K > T_{RKKY}$, the antiferromagnetic phase is replaced by a heavy fermion liquid (Coleman, 2007).

After the discovery of heavy fermion metals in 1975, Doniach proposed that their properties were the result of a dense lattice of magnetic moments, all screened by the Kondo effect (Doniach, 1977). A model of a lattice magnetic moments interacting with the conduction electrons had previously been worked out in the 1950s. The magnetic moments induce waves in the electron spin, which can then interact with other magnetic moments. This RKKY interaction, named after Ruderman, Kittel, Kasuya, and Yosida, usually leads to an antiferromagnetic ordering characterized by the energy k_BT_{RKKY} (Kasuya, 1956). Doniach proposed that when $T_K > T_{RKKY}$, which can occur at high coupling strength and carrier density, the Kondo effect could significantly change the properties. At low temperatures the magnetic moments would be a lattice of resonant scattering centers, with scattered electrons phase-shifted by a constant. Bloch wavefunctions would still be possible, but they would have to incorporate this resonant scattering, leading to a band of roughly the same width as the resonance, or $\sim k_BT_K$. This narrow band would have to have high curvature, leading to a high effective mass.

Measured properties

There are many heavy fermion superconductors to choose from, with a diversity of properties that is very large compared to the cuprates. Different heavy fermion superconductors may even be best described by different models of superconductivity. Still, there does seem to be a strong connection between heavy fermion materials and superconductivity, and there are a few general properties shared by heavy fermion superconductors. In this section the heavy fermion superconductors discussed have been selected to represent some of the diversity of properties, and the similarities have been left to appear on their own.

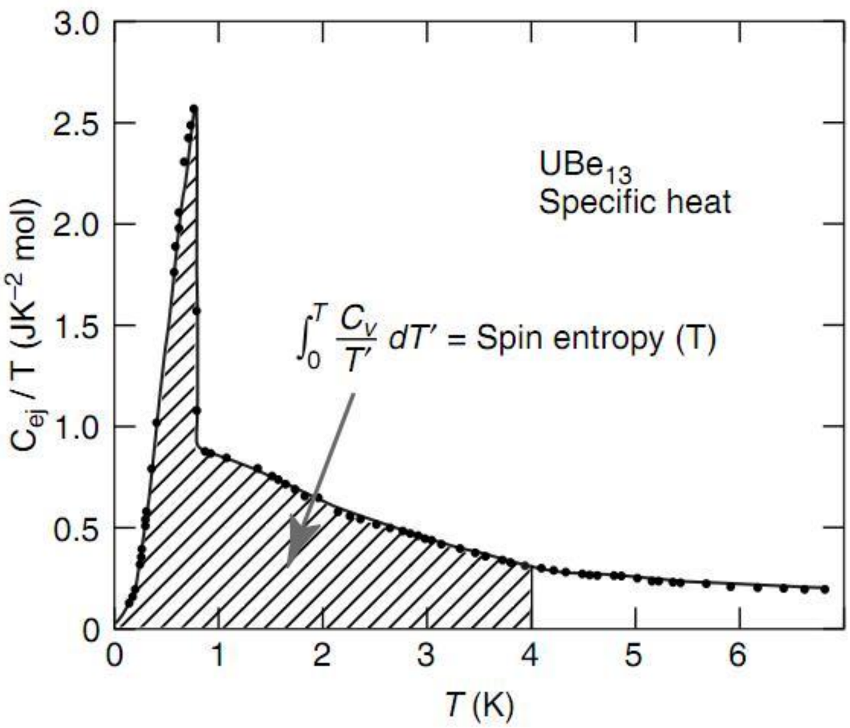
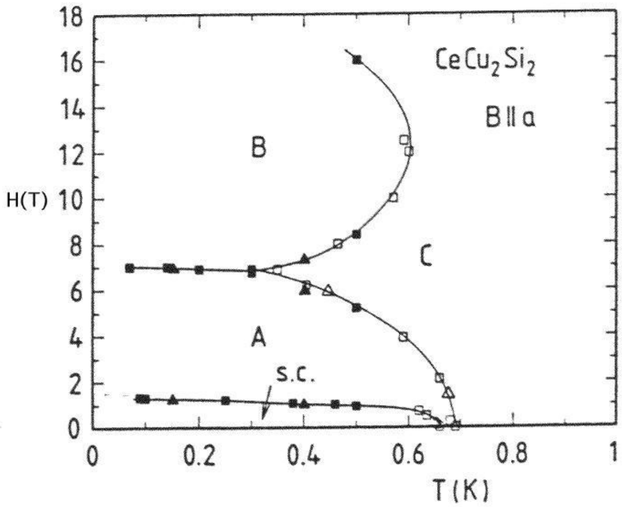


Fig. 2

The specific heat of UBe_{13} as it goes through its superconducting transition. If the superconducting state did not have heavy fermion properties, the specific heat below the jump would be much smaller (Coleman, 2007).

One general property of heavy fermion superconductors is that the superconducting electrons seem to be the same ones involved in the Kondo effect. Clear evidence for this is given by specific heat capacity measurements, because heat capacity is scaled by the effective mass of the quasiparticles. The specific heat capacity of heavy fermion superconductors jumps at T_C, but the scale remains set by the large effective mass of the quasiparticles (Coleman, 2007).

$CeCu_2Si_2$ was the first confidently observed heavy fermion superconductor, by Steglich et al. (Steglich et al., 1976). It has a Kondo temperature of approximately 10 K, and becomes superconducting at T_c = 0.7 K. Before the superconducting transition, it enters into an unusual “A phase” which has slow magnetic fluctuations, as measured by nuclear magnetic resonance and muon spin experiments. There is no nearby magnetically ordered phase, but the similarities under pressure to $CeCu_2Ge_2$ suggest that the material is just past being antiferromagnetic. The strong reduction in magnetic susceptibility below T_C signals a singlet pairing state. The symmetry of the order parameter is a bit unclear, with most low-temperature thermodynamic properties behaving as if the order parameter vanished along line nodes on the Fermi surface (Kuramoto and Kitaoka, 1999).



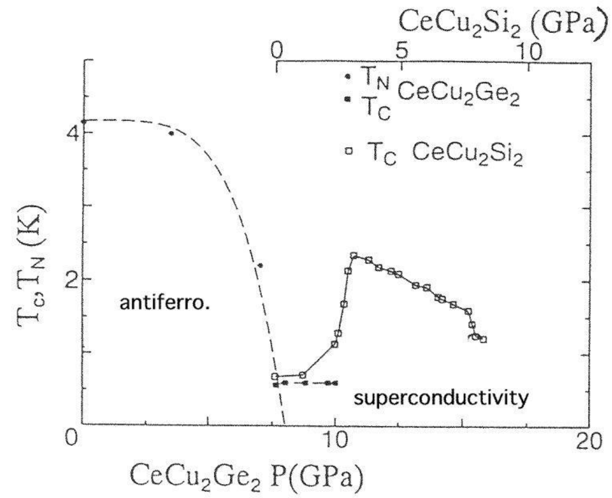


Fig. 3 and Fig. 4. The graph on the left shows the phase diagram of $CeCu_2Si_2$ under magnetic field. Note the ordered A phase that surrounds the superconducting phase. The graph on the right shows a comparison between $CeCu_2Si_2$ and $CeCe_2Ge_2$ under pressure – the rough similarity suggests that $CeCu_2Si_2$ starts out tuned past antiferromagnetic order (Kuramoto and Kitaoka, 1999).

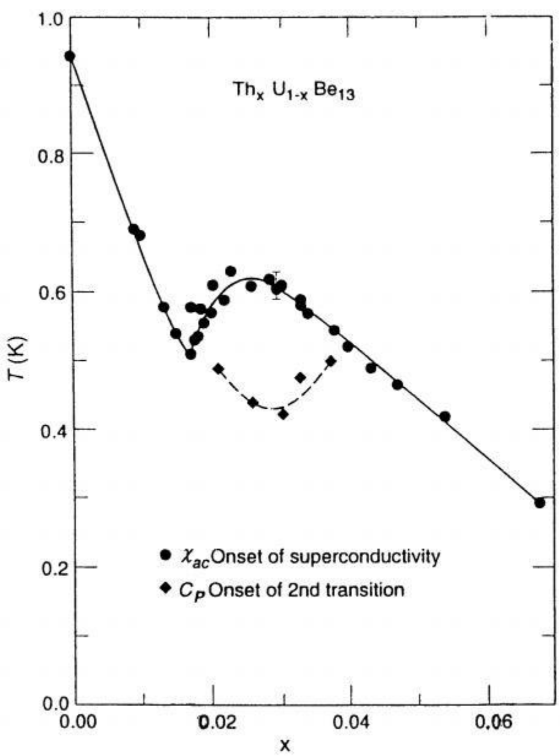


Fig. 5 shows the unusual behavior of UBe_{13} under doping with thorium. When 0.19<x<0.4, UBe_{13} has a poorly understood second phase transition (Kuramoto and Kitaoka, 1999).

UBe_{13} has a cubic crystal structure dominated by huge uranium atoms, with a T_C of 0.86 K (Ott et al., 1983). Like $CeCu_2Si_2$, and like another uranium-containing heavy fermion superconductor UPt_3, UBe_{13} is not near any magnetically ordered states, and unlike in $CeCu_2Si_2$ there is no additional reason to think that magnetism is close by even in an inaccessible way. Because of an inconclusive shift in magnetic susceptibility and a very high upper critical field, the pairing state is likely spin-triplet. Specific heat and NMR measurements disagree about the type of nodes in the order parameter, suggesting line and point nodes respectively. When doped with thorium, the T_C of UBe_{13} decreases up to a point, then increases temporarily when it enters an unusual region where there are actually two phase transitions. The normal state of UBe_{13} is unusual, with some non Fermi liquid properties predicted by a high-entropy “incoherent metal” model (Kuramoto and Kitaoka, 1999).

$CeIn_3$ was the first discovered “quantum critical” heavy fermion superconductor (Walker et al., 1997). Normally it forms antiferromagnetic order at temperatures below 10 K, but as pressure is increased the antiferromagnetic transition temperature goes to zero. Near the projected quantum critical point, the properties of the normal state no longer scale with temperature as predicted by the Fermi liquid model, and indication of the quantum critical region. Superconducting order in $CeIn_3$ forms a dome centered on the quantum critical point, with T_c = 0.2 K at 2.5 GPa (Mathur et al., 1998). The pairing state is singlet, and the order parameter has line nodes on the Fermi surface (Coleman, 2007).

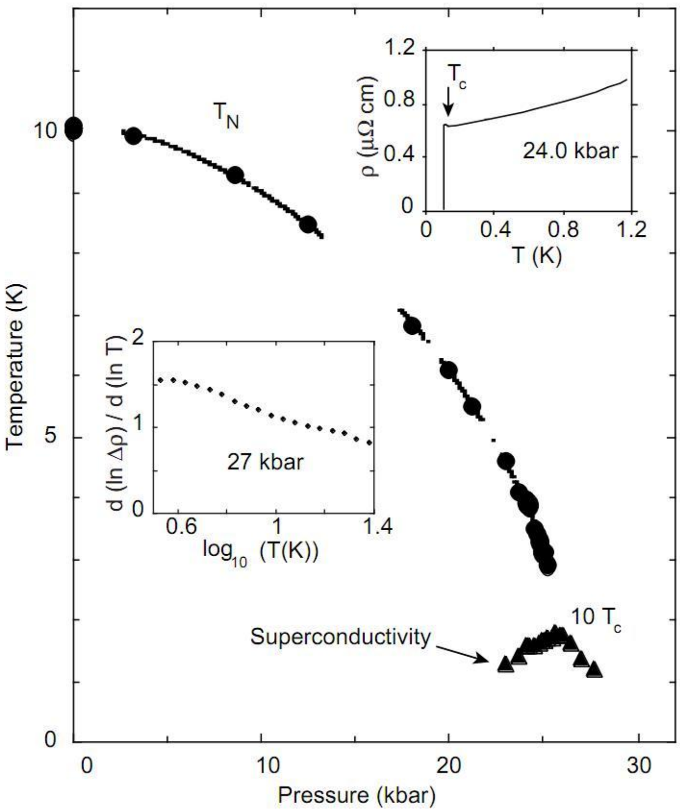


Fig. 6.

The phase diagram of $CeIn_3$ under pressure. As the antiferromagnetic transition temperature T_N goes to zero near 25 kbar (2.5 GPa), a superconducting phase appears (Mathur et al., 1998).

$CeCoIn_5$ was the first of the "1-1-5" class of heavy fermion materials. It has a layered structure, with conduction occurring in layers that are similar to $CeIn_3$. This type of structure had been predicted to enhance T_C, and so it did, to 2.3 K under no pressure and 2.6 K under 1.3 GPa (Petrovic et al., 2001). The phase diagram actually starts to resemble that of the cuprates, with a pseudogap regime appearing below optimal pressure. $CeCoIn_5$ exhibits no magnetic order, but like for $CeCu_2Si_2$ there are speculations about antiferromagnetic order at "negative pressure," based in analogy to the related material $CeRhIn_5$. The normal state of $CeCoIn_5$ is non Fermi liquid, similar to $CeIn_3$ (Sidorov et al., 2002). The pairing state is singlet, and the symmetry of the order parameter is probably d_{x2-y2}, in the superconducting planes (Coleman, 2007).

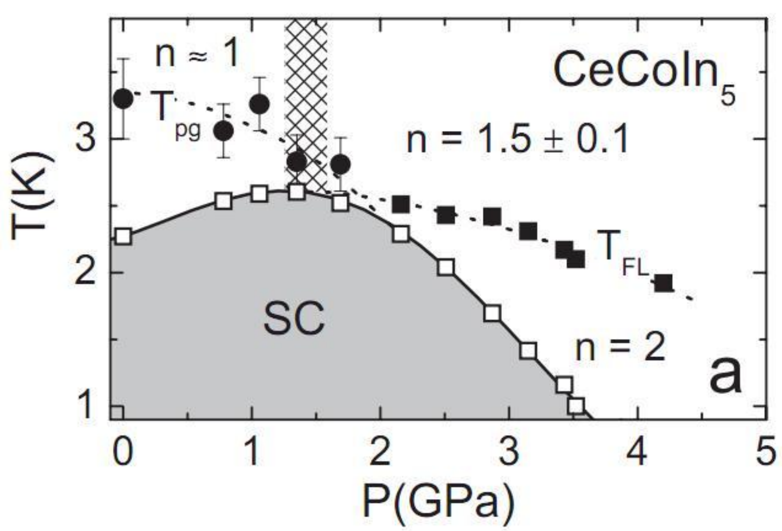


Fig. 7.

The phase diagram of $CeCoIn_5$ under pressure. Below T_{pg}, the system seems to be in a pseudogap state analogous to the cuprates. Below T_{FL}, the system is in a heavy Fermi liquid state. Above T_{FL} and T_{pg}, the system is in a non Fermi liquid normal state. (Sidorov et al., 2002).

Another notable 1-1-5 material is $PuCoGa_5$, which has the very high T_C of 18.5 K. Possibly because T_C is roughly as large as the Kondo temperature, $PuCoGa_5$ makes a direct transition from normal metal to heavy fermion superconductor. No evidence for a nearby magnetically ordered state was found (Serrao et al., 2002). Similar to $CeCoIn_5$ it forms singlet pairs, and has line nodes in the order parameter (Coleman, 2007).

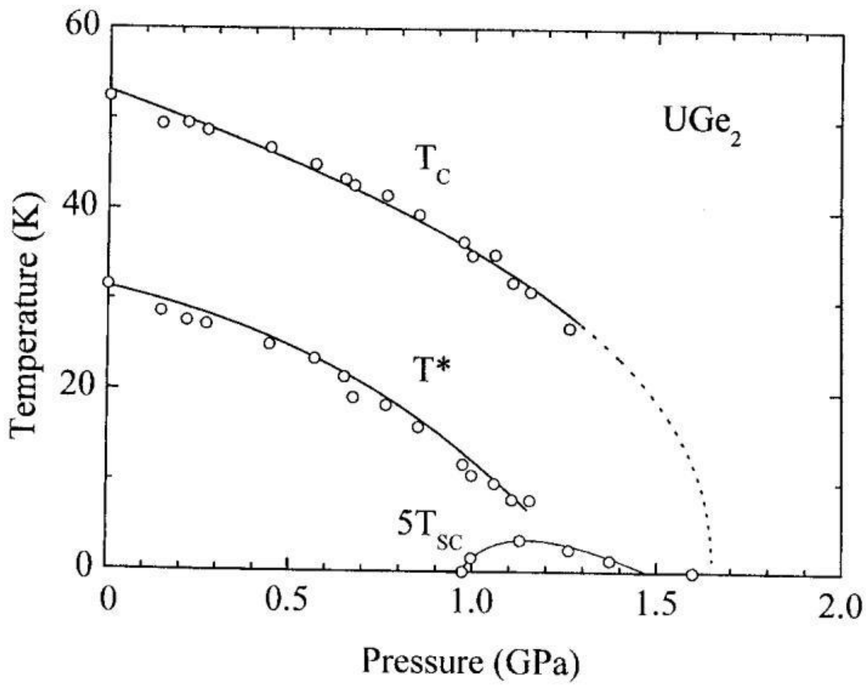


Fig. 8.

The phase diagram of UGe_2 under pressure. T_C is the ferromagnetic transition temperature, while T* is an transition in electronic order. The superconducting dome appears around the quantum critical point of T*, within the ferromagnetic region (Teitawa et al., 2001).

UGe_2 is interesting because it has ferromagnetic order rather than the usual antiferromagnetic order. It reaches a maximum T_C of 0.7 K at 1.1 GPa. UGe_2 appears to be a quantum critical superconductor, but the quantum critical point is not the disappearance of ferromagnetic order. Instead, there's some sort of electronic order that appears to go to zero at the maximum T_C. The heavy fermion superconducting state appears to coexist with ferromagnetism, making a triplet pairing state likely (Tateiwa et al., 2001). Antiferromagnetic ordering has also been observed to coexist with the superconducting state, in the heavy fermion superconductor URu_2Si_s (Kuramoto and Kitaoka, 1999).

Theoretical approaches

Three papers in 1986 introduced the idea of spin fluctuations as a pairing mechanism for the superconducting state. A key prediction of this model is that ferromagnetic interactions should lead to triplet pairing, while antiferromagnetic spin fluctuations should lead to singlet pairing, but not in the ordinary s-wave state. This materials this model best describes have nearby phase transition to a magnetically ordered state, which allows large spin fluctuations. Spin fluctuations can also grow if the density of magnetic moments reaches some critical value (Mathur et al., 1998), which fits reasonably well the heavy fermion superconductor UPt_3, which has antiferromagnetic spin fluctuations but no nearby phase transition (Coleman, 2007).

Anderson, in 1987, proposed the resonating valence bond (RVB) model as a mechanism for high T_C superconductivity. The Kondo lattice is described as a liquid of bonds between spins, which can "escape" into conduction electrons to promote the formation of superconductivity. The RVB model predicts a nearby magnetically ordered state, with no s-wave pairing possible (Coleman, 2007). The spin fluctuation approach naively supports the coexistence of magnetism and superconductivity, while in the RVB model, the magnetically ordered state would "melt" into a superconducting spin liquid (Anderson, 1987).

Given the placement of superconductivity in heavy fermion superconductors such as $CeIn_3$ and UGe_2, it is reasonable to speculate that quantum critical points can provide an environment for superconductivity. Near quantum critical points, phase fluctuations within the material expand in both space and time, and it has been suggested that these order fluctuations could provide the interaction to form Cooper pairs. This makes similar predictions to the spin fluctuation model near quantum critical points of magnetic order, but is more general - for example, in UGe_2, superconductivity appears near the projected disappearance of electronic order. The hope is that the pairing interaction could actually come from quite general properties of quantum critical fluctuations, similar to how ordinary critical matter acquires universal properties (Coleman, 2007).

There are, however, exceptions to all of the above proposals that suggest that there is no simple model of superconductivity heavy fermion materials. UGe_2, among other quantum critical heavy fermion superconductors, has properties that appear incompatible with the spin fluctuation or RVB models. UBe_{13} does not behave like a quantum critical material. $PuCoGa_5$ demonstrantes some sort of link between the superconducting and heavy fermion states, and is generally unusual.

So if the above models are incomplete, why is superconductivity common among heavy fermion materials? One reasonable guess is that, though incomplete, at least some of the above pairing mechanisms still work, and the electron-electron interactions that lead to the Kondo effect dominating the RKKY interaction simply lead to a lot of quantum critical points and magnetic phase transitions. A more exciting option would be a direct link between the heavy fermion state and superconductivity, perhaps through enhancement of the above proposals, or perhaps through some unknown mechanism. Evidence of this second option might be obtained by searching for unusual correlations between depressing T_K and depressing T_C.

References

Coleman, P. *Heavy Fermions: Electrons at the Edge of Magnetism.* Handbook of Magnetism and Advanced Magnetic Materials (2007)

Steglich, F., Aarts, J., Bredl, C.D., Lieke, W., Meschede, D., Franz, W., Schäfer, H., *Superconductivity in the Presence of Strong Pauli Paramagnetism:* $CeCu_2Si_2$. Phys. Rev. Lett. (1979)

Anderson, P.W., *Localized Magnetic States in Metals*. Phys. Rev. (1961)

Kondo, J., *Resistance minimum in dilute magnetic alloys*. Progress of Theoretical Physics (1964)

Doniach, S. *The Kondo lattice and weak antiferromagnetism*. Physica B+C (1977)

Kasuya, T., *A Theory of Metallic Ferro- and Antiferromagnetism on Zener's Model*. Progress of Theoretical Physics (1956)

Kuramoto, Y., Kitaoka, Y., *Dynamics of Heavy Electrons*. Preprint, Oxford University Press (1999)

Ott, H.R., Rudigier, H., Fisk, Z., Smith, J.L., *UBe_{13}: An Unconventional Actinide Superconductor*. Phys. Rev. Lett. (1983)

Walker, I.R., Grosche, F.M., Freye, D.M., Lonzarich, G.G., *The normal and superconducting states of $CeIn_3$ near the border of antiferromagnetic order*. Physica C: Superconductivity (1997)

Mathur, N.D., Grosche, F.M., Julian, S.R., Walker, I.R., Freye, D.M., Haselwimmer, R.K.W., Lonzarich, G.G., *Magnetically mediated superconductivity in heavy fermion compounds*. Nature (1998)

Petrovic, C., Pagliuso, P.G., Hundley, M.F., Movshovich, R., Sarrao, J.L., Thompson, J.D., Frisk, Z., Monthoux, P., *Heavy-fermion superconductivity in $CeCoIn_5$ at 2.3 K*. J. Phys.: Condensed Matter (2000)

Sidorov, V.A., Nicklas, M., Pagliuso, P.G., Sarrao, J.L., Bank, Y., Balatsky, A.V., Thompson, J.D., *Superconductivity and Quantum Criticality in $CeCoIn_5$*. Phys. Rev. Lett. (2002)

Sarrao, J.L., Morales, L.A., Thompson, J.D., Scott, B.L., Stewart, G.R., Wastom, F., Rebizant, J., Boulet, P., Colineau, E., Lander, G.H., *Plutonium-based superconductivity with a transition temperature above 18 K*. Nature (2002)

Tateiwa, N., Kobayashi, T.C., Hanazono, K., Amaya, K., Haga, Y., Settai, R., Ōnuki, Y., *Pressure-induced superconductivity in a ferromagnet UGe_2*. J. Phys.: Condensed Matter (2001)

Anderson, P.W., *The Resonating Valence Bond State in La2CuO4 and Superconductivity*. Science (1987)