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Superconductivity at the Border with Magnetism

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1. HISTORY

It was known well before the Bardeen, Cooper, and Schrieffer (BCS) theory of superconductivity that magnetic impurities in superconducting materials could cause large depressions in superconducting transition temperatures. But the first experiments where the systematics of the depression of superconductivity by magnetic impurities could be quantified were only carried out in 1958 by Matthias et al. in rare-earth-doped fcc lanthanum (La) [1] (Fig. 3.1). Rare earths carry a 4f local moment given by Hund's rules. It had been supposed prior to the experiment that the depression of T_c might vary with the effective moment carried by the rare-earth impurity. This proved not to be the case. Rather the depression followed the spin S of the 4f ground state (Fig. 3.2), varying as the square of its projection on the total angular momentum J of the 4f ground state $(J \cdot S)^2$, as recognized immediately by Suhl.

This result had a simple explanation within the then recent BCS theory of superconductivity. If the interaction between a conduction electron spin s and the 4f local moment spin on the impurity atom S is supposed of the form $H_{\text{int}} = -2J_{\text{int}} \mathbf{S} \cdot \mathbf{s} = -2(g-1)J_{\text{in}} \mathbf{J} \cdot \mathbf{s}$, where the Landé g -factor provides the projection of S on J , then the local moment spin S will interact with opposite sign on the two spins of a Cooper pair, depressing T_c in proportion

Figure 3.1 Depression of the superconducting transition temperature of fcc La by 1 at% addition of rare earth [1].

Figure 3.2 Spin (S) and effective moment μ_{eff} of the Hund's Rule ground state of rare earths.

to the so-called deGennes factor $(g-1)^2 J(J+1)$. The detailed theory was worked out by Abrikosov and Gor'kov [2], and this theory when account is taken of crystal field effects gives a good description of experiment for the entire superconducting range of compositions in the numerous intermetallic superconductors where this has been studied. Representative data are shown in Fig. 3.3.

Figure 3.3 Depression of superconducting T_c and antiferromagnetic T_N in alloys of $Gd_xEr_{1-x}Rh_4B_4$ [3].

2. TERNARY MAGNETIC SUPERCONDUCTORS

Ginzburg (1957) [4] was the first to point out that superconductivity and ferromagnetism were incompatible. The depression of T_c experiments reported by Matthias et al. in 1958 included a study of superconductivity and ferromagnetism as well (Fig. 3.4) in the binary La–Gd alloy system, which appeared to be consistent with this claim.

A number of intermetallic systems were subsequently investigated similarly via alloying between isostructural superconducting and ferromagnetic end members where the magnetic exchange coupling J_{int} appeared to be very weak, but without any convincing evidence of the coexistence of superconductivity and long-range magnetic order. But the study of the coexistence of superconductivity and magnetic order took a new turn with the discovery of superconductivity in the rare-earth ternary compounds RMo_6X_8 ($X = S, Se$; $R = \text{rare earth}$) (1975, 1976) [5], known as Chevrel phases, and RRh_4B_4 (1977) [6], compounds which possess a stoichiometric sublattice of rare-earth ions. Matthias had earlier (1972) reported the discovery of superconductivity at 13.7 K in $PbMo_6S_8$ [7], but it was very much a surprise when Fischer et al. reported superconductivity in a number of the isostructural materials with rare-earth atoms in place of Pb. While the T_c 's found were in the range of 1 K without sign of magnetic order as measured by magnetic susceptibility down to

Figure 3.4 Variation of superconducting (T_c) and ferromagnetic Curie temperatures (T_{Curie}) in $\text{La}_{1-x}\text{Gd}_x$ alloys [1].

this temperature, one nevertheless wondered what was happening to the rare-earth 4f magnetic moments, particularly in the cases where Kramer's theorem told you that the crystal field ground state of the 4f electrons could not be a singlet. It was soon discovered that a number of the rare-earth Chevrel phases as well as the rare-earth rhodium borides supported coexisting superconductivity and antiferromagnetic order (Fig. 3.5). Furthermore, a reentrant superconductivity was discovered in HoMo_6S_8 and in ErRh_4B_4 (Fig. 3.6) where a higher temperature superconducting state was quenched by a lower T_c ferromagnetic ordering. The experimental observation that the establishment of ferromagnetic order quenched superconducting order in both HoMo_6S_8 and ErRh_4B_4 was consistent with the prediction of Ginzburg. That antiferromagnetic order could coexist with superconductivity could be rationalized with the observation that the antiferromagnetic exchange field could average to zero over the superconducting coherence length. And the antiferromagnetic ordering was not without effect on the superconducting state, there being clearly observed effects on the upper critical fields of these type II superconductors.

In a certain sense, these ternary magnetic superconductors are like dilute alloys in that the weak conduction electron—4f local moment interaction allows one to think of the 4f moments as a weak perturbation to the conduction electron system. The important aspect of these compounds, however, is

Figure 3.5 Superconductivity (sc) and magnetism (square symbols) in rare-earth RRh_4B_4 [8]. The square symbols are antiferromagnetic (open) and ferromagnetic (solid) ordering temperatures.

Figure 3.6 Magnetic susceptibility (χ) and electrical resistance (R) of the reentrant superconducting transition in $ErRh_4B_4$ [8].

that the rare earths sit on a chemically ordered sublattice that can support a low-temperature magnetic state with long-range order. In addition to the Chevrel and rare-earth rhodium boride materials discussed above, a number of other similar systems have been discovered, most importantly the rare-earth $\text{RNi}_2\text{B}_2\text{C}$ compounds, which can be grown fairly easily as high-quality single crystals from Ni-In molten flux and which have enabled as a result of careful investigation of important details regarding the interaction of magnetism and superconductivity not easily pursued in polycrystalline material [9].

3. KONDO IMPURITIES

The original experiments on the depression of T_c by rare-earth impurities in La (Fig. 3.1) were shown to be consistent with a conduction electron-local moment interaction J_{int} , which varied only slowly with rare earth provided account was taken of crystal field effects on the Hund's rule 4f ground state, with one exception, Ce. Ce is seen to have an anomalously large depression of T_c relative to its position in the rare-earth series. Ce is the first rare earth with an occupied 4f level, and it is not surprising that the situation here might be somewhat different since the 4f shell is only just becoming stabilized.

It turns out that the physics of Ce is quite different than that of the heavier rare earths, that it alone among the rare earths dissolved in La has $J_{\text{int}} < 0$, an antiferromagnetic interaction, whereas all the other rare earth have $J_{\text{int}} > 0$, a ferromagnetic interaction. This was shown in experiments by Sugawara and Eguchi (1966) [10] where Ce-doped La was shown to exhibit an electrical resistivity minimum at low temperatures, consistent with the then very recent theoretical explanation of resistivity minima in dilute magnetic alloys by Kondo (1964) [11]. Kondo provided an answer to a long-standing puzzle in the low-temperature electrical resistivity of alloys with magnetic impurities. He showed that the resistivity minimum observed in a number of transition metal alloys could be explained in second Born approximation if J_{int} was antiferromagnetic, predicting a low-temperature rise in the electrical resistivity $\Delta\rho \sim -\ln T$ as observed. While this theory was developed with transition metal impurities in simple metal hosts in mind, it was evident from the experiments of Sugawara and Eguchi that Ce impurities in La were to be classed as Kondo ions.

The reason that Ce differs from the other rare-earth impurities dissolved in La is a result of the unstable nature of the 4f¹ state. Friedel [12] had developed the concept of the virtual bound state to explain various magnetic and electrical properties of transition metal ions, the idea being that the d level

of a transition metal atom dissolved in a metallic host might have this level coincident in energy with conduction electron states of the host metal. Since a bound d state cannot exist in such a case, Friedel suggested that the impurity d level could be thought of as a resonant state that had been broadened by hybridization with conduction electron states. If this broadening was not too great, some atomic-like properties might persist. Anderson developed subsequently an impurity model which formalized the ideas of Friedel [13]. Schrieffer and Wolff [14] then showed how in the limit of weak hybridization, one could derive the effective conduction electron-local moment spin Hamiltonian $H_{\text{int}} = -2J_{\text{int}}\mathbf{S}\cdot\mathbf{s}$, where $J_{\text{int}} = |V_{\text{kd}}|^2 U / (\epsilon_d (\epsilon_d + U)) < 0$. In this expression, V_{kd} is the hybridization matrix element between the conduction electrons and the d level at energy ϵ_d with respect to the Fermi level and U is the Coulomb repulsion between the two electrons in the 4f level, and is large and positive. These are the parameters in the Anderson impurity model which determine whether an impurity is magnetic. This theory applies equally well with 4f electrons in a virtual bound state. For the case of well-localized 4f electrons where the 4f energy lies well below the conduction band, J_{int} is given by the Coulomb exchange integral and this is always positive. It is the closeness of the energy of the Ce 4f level to the Fermi level, its weakly bound character, that gives rise to its Kondo behavior.

The Kondo impurity presented a difficult theoretical problem which was finally formally solved by Wilson using renormalization group methods [15]. For $J_{\text{int}} < 0$, the conduction electrons form into a collective singlet with the local moment below a characteristic Kondo temperature $k_B T_K \sim (1/\rho) \exp(1/\rho J_{\text{int}})$, where ρ is the electronic density of states at the Fermi level. As temperature decreases below T_K , the entropy associated with the local moment spin degrees of freedom become shared with the conduction electrons and give rise to an enhanced conduction electron mass reflected in a contribution to the low-temperature electronic specific heat coefficient $\gamma \sim k_B \ln 2 / T_K$ per impurity. Over this same range of temperature, the high-temperature Curie-Weiss magnetic susceptibility characteristic of local moments evolves into a temperature-independent Pauli paramagnetism with magnitude consistent with the electronic specific heat γ .

Following the work of Sugawara and Eguchi, a number of intermetallic superconductors were investigated where it was found that rare-earth additions depressed T_c in similar fashion as in elemental La, with again Ce often being anomalous and associated with Kondo behavior (Figs. 3.7 and 3.8). A further question arose as to how the depression of T_c (ΔT_c) might vary if one could tune the hybridization V_{kf} through the regime from magnetic to

Figure 3.7 Depression of the superconducting transition temperature of YB_6 ($T_c = 6.0$ K) by rare-earth impurities [16].

Figure 3.8 Low-temperature electrical resistivity of Ce-doped YB_6 plotted against $\ln T$.

nonmagnetic behavior of the impurity ion. It turns out that one can accomplish this using applied pressure in the case of Ce impurities. The simple picture for this is that the $4f^1$ level of Ce is an inner level with small radial extent relative to the outer valence electrons of Ce. This means that an f electron screens quite effectively one nuclear charge, the outer valence electrons acting as if they were in an atom with one less proton in the nucleus. This makes the effective metallic radius of the Ce ion larger than it might be if

Figure 3.9 Superconducting T_c of $\text{La}_{1-x}\text{Ce}_x$ as a function of pressure [17]. Curves labeled by x .

the f level was unoccupied. The effect of applied pressure is then to try to push out the $4f$ electron from the atomic core, demagnetizing Ce as it were. Such an effect is seen in the experiments by Maple et al. (Fig. 3.9) on Ce-doped La. Here for 2 at.% Ce in La one sees that the pair breaking in the 10-kbar range has become sufficiently large to kill T_c , and that T_c recovers at higher pressures where Ce no longer has a local moment. With increasing pressure, a Kondo description of the Ce ion will no longer be appropriate, where the spin and charge aspects of the $4f$ level both become relevant to the physical properties as opposed to the spin-only physics of the Kondo effect. The regime where T_c and T_K become comparable has also received special attention, where it is found that materials can go from normal to superconducting to normal as a function of temperature in some cases.

4. DENSE KONDO SYSTEMS

A natural question arising in the study of Kondo impurity systems is what happens in materials where it is possible to vary the concentration of the Kondo ion to full occupation of the site. The study of Ce-doped superconductors led quickly to the realization that Kondo-like features

Figure 3.10 Electrical resistivity of the dense Kondo compound CeB_6 . The drop in resistivity at low temperature is due to a combination of quadrupolar and magnetic order [16].

persisted into the chemically fully ordered Ce intermetallics in many cases. This is evident in the electrical resistivity, as seen (Fig. 3.10), for example, in CeB_6 , the $x=1$ limit of the Kondo system $\text{Y}_{1-x}\text{Ce}_x\text{B}_6$ (Fig. 3.7). A clearer picture concerning what was going on in the dense Kondo materials started to emerge in 1976 with the discovery that the low-temperature specific heat γ of CeAl_3 (Fig. 3.11) had the value of $1.62 \text{ J/mol-Ce K}^2$, vastly larger than

Figure 3.11 Low-temperature specific heat of CeAl_3 [18].

Figure 3.12 Electrical resistivity of CeAl_3 [19].

that of a typical metal that is in the $1\text{--}10\text{ mJ/mol K}^2$ range [18]. Furthermore, the value was in reasonable accord with a free electron estimate of the measured Pauli-like paramagnetic susceptibility, suggesting that the low-temperature properties of CeAl_3 resembled those of a free electron metal with an enormous enhancement of the conduction electron effective mass. Typical of dense Kondo materials, the electrical resistivity of CeAl_3 (Fig. 3.12) passes through a maximum at a temperature generally referred to as the coherence temperature, below which metallic Bloch states characteristic of an ordered lattice of ions develop, as shown by a variety of physical measurements.

5. HEAVY FERMION SUPERCONDUCTIVITY

Dense Kondo materials generally have high-temperature Curie-Weiss magnetic susceptibilities corresponding to that expected from the Hund's rule $4f$ ground state. For Ce, this is the sixfold degenerate $J=5/2$ state. Yb ($4f^{13}$) also is often a Kondo ion, and here the Hund's rule ground state is the eightfold degenerate $J=7/2$. The crystalline environment of the $4f$ ion lifts the degeneracy of the Hund's rule ground state, typically in the case of Ce into three doublets (four doublets typically in the case of Yb), so that one is dealing at low temperature with a ground state doublet often well separated (but not necessarily so) from the higher lying doublets. The doublet carries a magnetic moment, and it is not surprising that Ce dense Kondo materials can order magnetically, particularly if the lattice coherence

Figure 3.13 Specific heat of single crystal nonsuperconducting ($\bullet$, $\square$) and polycrystalline ($\times$) of CeCu_2Si_2 [19,20].

temperature, below which the magnetic degrees of freedom become entangled with those of the conduction electrons, is low. It is common in such cases to see magnetic order happening at a peak in the electrical resistivity, since the lattice coherence has not yet set in.

Superconductivity might appear to be a less likely occurrence even when coherence is fully established, given the magnetic parentage of the coherent ground state. So it came as a shock when Steglich showed in 1979 that the dense Kondo material CeCu_2Si_2 was a bulk superconductor (Fig. 3.13) at 0.5 K [20]. One sees the specific heat jump characteristic of a second-order superconducting phase transition occurring with gap opening in a very high density of states band, $C/T \sim 0.75 \text{ J/mol-Ce K}^2$ at T_c . The electrical resistivity of this material (Fig. 3.14) is typical of a dense Kondo compound, showing Kondo features superimposed on changing populations of the crystal field levels, with coherence setting in below approximately 10 K.

There are several points to make about this result. The first is that the superconductivity had been seen in a number of earlier studies of this material but not believed because of its implausibility, rather thought to be due to some impurity phase. The compound is difficult to prepare as a bulk superconductor for metallurgical reasons, and it was essential to get this metallurgy correct to establish bulk superconductivity from specific heat data. Furthermore, a number of what were believed to be regular Ce-based BCS superconductors were already known, such as CeRu_2 ($T_c = 7.0 \text{ K}$) and CeCo_2 ($T_c = 1.5 \text{ K}$). The thinking for these was that Ce was in the tetravalent state or, equivalent at the time, the collapsed nonmagnetic state. There was no hint of high-temperature

Figure 3.14 Temperature variation of electrical resistance (in arbitrary units; room temperature resistivity of UBe_{13} is $100 \mu\Omega \text{ cm}$) of the heavy fermion superconductors CeCu_2Si_2 (triangles), UBe_{13} (squares), and UPt_3 (circles) [19].

magnetic behavior in the magnetic susceptibility of these compounds, neither were there any Kondo-type resistivity features. Finally, the very large value of γ suggests that very narrow bands are present at the Fermi surface with attendant strong electron correlations. The question then arises as to how Cooper pair formation can be favorable. Higher angular momentum pairing seems possible, which would have a wave function node at $r=0$, but such pairing was thought to be highly unlikely except in extremely clean metals, due to impurity quenching of the angular momentum. In fact, in the early days following BCS such superconductivity was looked for and not found in super pure samples of the almost magnetic metal Pd.

The label heavy Fermion superconductor was applied to CeCu_2Si_2 , coming about from a disagreement between Steglich and his postdoctoral advisor Wohlleben who was particularly distressed by this development in the field of superconductivity. No further Ce-based dense Kondo superconductors were immediately forthcoming despite a large effort to find them. Unexpectedly, the next development in heavy fermion superconductivity occurred not in 4f materials but in the 5f materials UBe_{13} and UPt_3 , with T_c 's of 0.9 and 0.5 K, respectively.

It is perhaps not so strange that superconductors in this class should be found among 5f materials. There are many similarities between 4f and 5f materials, but the 5f electrons are considerably more extended in space,

Figure 3.15 Low-temperature specific heat of UBe_{13} . The upper left inset shows the upper critical field as a function of temperature. The right inset shows the temperature-dependent inverse magnetic susceptibility and its high-temperature Curie-Weiss form [23].

intermediate in this between the fairly localized $4f$'s and the quite delocalized $3d$'s, and finding systems where dilute U impurities act like Kondo centers is not at all common. UBe_{13} , the first heavy fermion U-based superconductor (1983) [21], was chosen for study by Ott because he remembered that Bucher had seen what he regarded as filamentary superconductivity in it in 1975 [22]. Bucher had not measured the specific heat, and, as with CeCu_2Si_2 , superconductivity seemed so unlikely in this material. Large single crystals of UBe_{13} proved to be easily grown from Al flux, and specific heat measurements (Fig. 3.15) showed unequivocally that the material was a bulk superconductor with the gap opening in a very high density of states band. The electrical resistivity shown above in Fig. 3.14 has remarkable similarities to that of CeCu_2Si_2 .

To come to grips with this unusual superconductivity, much effort went into trying to find ways in which it showed differences with standard BCS behavior, for example, how did impurities influence T_c ? These data were surprising (Fig. 3.16). Not only did impurities carrying moments (Gd) not

Figure 3.16 Depression of the superconducting transition temperature of UBe_{13} by various impurities [24].

have effects much different from those without moments (La, Lu), but Th impurities produced a nonmonotonic depression, with a sharp cusp in T_c at 1.7 at.% Th [25]. Specific heat measurements then found (Fig. 3.17) that two phase transitions existed in samples with Th concentration greater than $x=0.017$. The lower transition was found not to be a magnetic transition

Figure 3.17 Low-temperature specific heat of $\text{U}_{0.967}\text{Th}_{0.033}\text{Be}_{13}$. The inset shows variation of T_c with Th concentration as measured resistively [23].

but rather a second superconducting transition. This had not been observed in any previous homogeneous materials and represented something quite new. While it seems possible that such a double transition might result from superconducting transitions on separate pieces of Fermi surface, this had never been known to occur, and a more likely explanation was that the superconducting order parameter is complex with more than one component. This was the indication that the superconductivity in these heavy fermion materials was of a new kind and immediately experiment was directed toward establishing this. Theorists had already been thinking about this in the context of the superfluidity of ^3He , where more than one superfluid phase was known to exist. The simple possibilities that presented themselves were spin triplet p-wave and spin singlet d wave, with various possibilities within these categories. A partial signature of these exotic pairings was possible nodes of the superconducting gap on the Fermi surface, either points or lines depending on the particular state, and such nodes would lead to power-law temperature dependences in various physical properties below T_c , such as specific heat, for example, in contrast to the exponential variation expected well below T_c in the case of BCS. Power laws in specific heat were observed (Fig. 3.18) as well as in other properties below T_c such as NMR relaxation rate $1/T_1 T$ and acoustic attenuation. Also observed were behaviors right at T_c not seen previously in superconductors

Figure 3.18 Log-log plot of low-temperature specific heat of UBe_{13} and various Th-doped alloys showing power law in T temperature dependence [26].

having to do with the so-called coherence factors, indicative of a non-BCS pairing. For example, a peak in acoustic attenuation at T_c was seen.

Shortly after the discovery of heavy fermion superconductivity in UPt_3 , a second U-based heavy fermion superconductor was discovered, UPt_3 with $T_c = 0.5 \text{ K}$ [27]. This material forms in the same crystal structure as the dense Kondo compound CeAl_3 , the hexagonal stacking of Cu_3Au , this being one reason why it was chosen for study. It grows as needle-like single crystals from Bi flux with residual resistivity ratios well in excess of 100, enabling extensive Fermi surface investigations, and shows well-characterized Landau Fermi liquid behavior. The initial specific heat measurements establishing bulk superconductivity showed a dome-like anomaly at T_c , which subsequent measurements on higher resistance ratio crystals established to be due to two closely spaced superconducting transitions (Fig. 3.19). As with UPt_3 , power-law temperature dependences below T_c in various properties suggested that the superconducting gap had nodes on the Fermi surface. Extensive ultrasonic and thermodynamic measurements in applied magnetic field were conducted on high-quality single crystals, establishing a superconducting phase diagram which bears some similarities to what is seen in ^3He (Fig. 3.20), with the presence of multiple superfluid phases. Three superconducting phases appear in the H - T phase diagram. The low-temperature phase found in zero field has a line of nodes of the gap on the Fermi surface in the basal plane and point nodes along the

Figure 3.19 Low-temperature specific heat of high-purity polycrystalline UPt_3 showing the two superconducting phase transitions [28].

Figure 3.20 Phase diagram of UPt_3 in the applied external magnetic field (H)–temperature plane [29]. Field applied parallel to the crystallographic c -axis.

hexagonal z -axis. The detailed description of these phases still remains to be completely worked out.

While the early attention in heavy fermion superconductivity centered on CeCu_2Si_2 , UPe_{13} , and UPt_3 , there remained in the background a mysterious superconducting antiferromagnet, URu_2Si_2 , crystallizing in the same structure as CeCu_2Si_2 . Antiferromagnetic order sets in below 17.5 K, followed by superconductivity below 1.2 K. The antiferromagnetic order, however, involves only a sublattice magnetization of $0.03\mu_B$, in spite of a large heat capacity anomaly at T_N . This has led to the suggestion that the upper 17.5 K transition involves some kind of hidden order, which the small ordered moment is a symptom of. Extensive experimental work has been done on this system, including pressure studies (Fig. 3.21) which find that the hidden order gives way beyond 0.7 GPa to a magnetically ordered large moment ($0.4\mu_B$) phase, with superconductivity only coexisting with the hidden order phase. The electronic specific heat $\gamma \approx 180 \text{ mJ/mol-UK}^2$ at T_N , with integrated entropy up to T_N of $\Delta S \approx 0.2R \ln 2$. At the superconducting T_c , $\gamma \approx 60 \text{ mJ/mol-UK}^2$. The γ value at T_N clearly places this material in the heavy fermion category, and the HO ordered moment in light of the substantial fraction of $R \ln 2$ developed by T_N points to physics differing from that seen in usual antiferromagnetic ordering. One viewpoint on the coexistence of superconductivity with the hidden order is that these two phases are competing for the Fermi surface. This is a quite different viewpoint than that which appears appropriate for the Chevrel phases and

Figure 3.21 Pressure-temperature phase diagram of URu_2Si_2 . HO, LMAF, PM, and S denote hidden order, large moment antiferromagnetism, paramagnetism, and superconductivity, respectively [30].

rare-earth rhodium borides, where local moment magnetism is thought to coexist with superconductivity of conventional nature.

Two other heavy fermion U-based materials supporting both antiferromagnetism and superconductivity occur in the hexagonal CaCu_5 structure: UNi_2Al_3 ($T_N=4$ K, $T_c=1$ K)[31] and UPd_2Al_3 ($T_N=14.5$ K, $T_c=2$ K) [32]. Their respective γ 's at T_N are 150 and 125 mJ/mol-UK², respectively. Both appear to have cylindrical pieces of Fermi surface, characteristic of 2D behavior. In UNi_2Al_3 the magnetic order is an incommensurate spin density wave with amplitude $0.2\mu_B$; in UPd_2Al_3 it is a commensurate antiferromagnetic ordering with ordered moment $0.8\mu_B$. In the Ni compound, the superconducting pairing is believed to be of triplet type, in the Pd material singlet.

The idea slowly developed during the 1990s that the heavy fermion superconductors all had a nearby magnetic phase. This idea came from thinking about the effects of pressure on Ce-based materials in the context of the Doniach phase diagram (Fig. 3.22) [33]. The coupling of conduction electrons to Ce local moments with strength ρJ_{int} produces two energy scales in the dense Kondo lattice, the Kondo scale $k_B T_K \sim \rho^{-1} \exp(-1/\rho J_{\text{int}})$ and the Ruderman-Kittel-Kasuya-Yoshida (RKKY) 4f moment-moment interaction $k_B T_{\text{RKKY}} \sim \rho J_{\text{int}}^2 F$ determining magnetic ordering temperature, where F contains factors specific to the lattice and not dependant

Figure 3.22 Doniach phase diagram. The upper panel shows evolution of RKKY and Kondo scales with $|J| = \rho J_{\text{int}}$. The lower panel shows dome of antiferromagnetic order with a quantum critical point $T_N \rightarrow 0$ K at a critical J_c .

on J_{int} . For small ρJ_{int} the RKKY dominates and magnetic order is the ground state. Beyond some critical value of (ρJ_{int}) the Kondo scale will dominate. The simple idea was that superconductivity might be favored in the critical region and that one could access this region in Ce-dense Kondo systems using applied external pressure (Fig. 3.23).

Figure 3.23 Hypothetical inclusion of superconducting phase (SC) into Doniach phase diagram.

This proved to be the case. The first example was the finding of superconductivity under pressure in the 35 K antiferromagnet CeRh_2Si_2 below 400 mK near 0.9 GPa, where the Néel temperature had been suppressed close to 0 K [34]. More detailed studies followed on CeIn_3 and CePd_2Si_2 (Fig. 3.24) [34], supporting the hypothesis that probably all the heavy fermion superconductors might lie in the region indicated in Fig. 3.23. This line of thinking also encouraged the idea that the pairing mechanism in heavy fermion superconductivity was of magnetic origin. It is worth noting that establishing the pairing mechanism is not directly accessible to experiment but that establishing the superconducting gap structure over the Fermi surface is.

The search for superconductivity near the magnetic quantum critical point in the Doniach phase diagram increased substantially the number of known heavy fermion superconductors. At about the same time, a new system of heavy fermion materials was uncovered, the isostructural, isoelectronic sequence CeCoIn_5 ($T_c = 2.3$ K), CeRhIn_5 ($T_N = 3.9$ K), and CeIrIn_5 ($T_c = 0.4$ K) [36]. These tetragonal materials are quite easily grown as single crystals from In flux with very high residual resistance ratios, allowing extensive detailed studies. Single crystals can also be grown of mixed members of the series (Fig. 3.25), and superconductivity is found to coexist with antiferromagnetism in some ranges of solid solution. Exactly how to describe this coexistence is not known, but NMR measurements suggest the coexistence is homogeneous. An interesting observation

Figure 3.24 Temperature-pressure phase diagram of CePd_2Si_2 [35]. AFM and SC denote antiferromagnetism and superconductivity, respectively.

Figure 3.25 Phase diagram of binary alloys across the CeRIn_5 series ($R = \text{Co}, \text{Rh}, \text{and Ir}$) [37].

concerning this alloy phase diagram is that there is no coexistence when superconductivity occurs first on cooling.

Extensive studies have been made on the 3.9-K antiferromagnet CeRhIn_5 as a function of pressure (Fig. 3.26) [38]. Heavy fermion superconductivity develops with pressure, and as in the alloy case, coexists with

Figure 3.26 Temperature–pressure phase diagram of CeRhIn_5 . P_2 is the extrapolated quantum critical point where $T_N = 0 \text{ K}$ [38].

antiferromagnetism until the T_c becomes larger than the T_N near 1.8 GPa. T_c just beyond 2.0 GPa increases to a maximum of 2.3 K, the same T_c as found in CeCoIn_5 at ambient pressure. One can extrapolate to a $T_N=0$ K quantum critical point in the phase diagram $P_2=2.3$ GPa. And de Haas-van Alphen measurements find that the Fermi surface of CeRhIn_5 changes beyond this pressure into a larger one that is similar to that found in CeCoIn_5 , from a Fermi surface that is similar to that of LaRhIn_5 and LaCoIn_5 [39]. The implication of this is that the Ce 4f electron has delocalized and been incorporated into the Fermi surface of both CeCoIn_5 at ambient pressure and CeRhIn_5 beyond $P_2=2.3$ GPa. In this regard, we note that these materials have a quasicylindrical piece of Fermi surface suggestive of 2D electronic character, plus other 3D Fermi surface pieces. Neutron-scattering measurements do not find characteristics of 2D magnetic correlations in CeRhIn_5 .

It has been proved possible with doping on the In sites in CeCoIn_5 to induced antiferromagnetic order (Fig. 3.27). There are two inequivalent In sites in CeCoIn_5 , but X-ray Absorption Fine Structure (XAFS) measurements have shown that Cd substitutes on both these sites. These data demonstrate that superconducting CeCoIn_5 lies in fact very close to a magnetically ordered ground state. Also interesting is that pressure can exactly undo the effect of Cd doping (Fig. 3.28). A simple conjectured explanation of this is that Cd substituted for In in CeCoIn_5 induces the 4f electrons of its near neighbor Ce ions to become more localized, and this more localized Ce is enough to shift the balance to a magnetic ground state. Applied pressure will have the largest effect on these more compressible Ce ions, so that pressure is able to easily reverse the effect of Cd doping. What is particularly interesting is that it is possible with a simple shift of the pressure axis to superimpose the temperature–pressure phase diagram of pure CeRhIn_5 on that of Cd-doped CeCoIn_5 [40].

Figure 3.27 Effect of Cd doping on CeCoIn_5 . Actual concentration of x is 0.10 times the nominal concentration that was in the crystal growth melt [40].

Figure 3.28 Temperature–pressure phase diagram of Cd-doped CeCoIn_5 compared with CeRhIn_5 . For the Cd-doped alloys, the pressure axis has been rigidly shifted to get coincidence of the curves [40].

Single crystals of CeCoIn_5 can be grown with residual resistivities in the few tens of the $\text{n}\Omega\text{-cm}$ range. This fact has encouraged a search for a modulated superconducting state in applied magnetic field known as the Fulde–Ferrel–Larkin–Ovshnikov (FFLO) [41] state which has never been observed. Theory suggests that it could only be observed in extremely clean

Figure 3.29 Temperature–magnetic field low-temperature phase diagram of CeCoIn_5 produced from specific heat measurements showing presence of new phase line below H_{c2} below 400 mK [42].

material. Experiments in CeCoIn_5 (Fig. 3.29) have looked for this state and discovered evidence for a new phase within the superconducting phase. It is not clear at present whether this is the FFLO phase. In particular, exactly what the definitive diagnostic for the FFLO phase is in a real material is not settled.

A number of actinides form compounds with the tetragonal 115 structure. None of the U-based materials with this structure were found to be superconducting (Fig. 3.30), but remarkably, the first known Pu superconductors were found in it with the astonishing T_c 's of 18.6 K for PuCoGa_5 and 8.5 K for PuRhGa_5 [43]. Subsequently, the first Np-based superconductor was found in a related tetragonal structure with $T_c = 4.9$ K, NpPd_5Al_2 [44]. These three materials all are moderately enhanced heavy fermion materials with $\gamma \sim 100 \text{ mJ/mol K}^2$ for the Pu materials, 200 mJ/mol K^2 for the Np compound.

One further Ce-based superconductor is CePt_3Si [45]. This compound is a $T_N = 2.2$ K antiferromagnetic with coexisting superconductivity below $T_c = 0.75$ K. What is novel here is that this is the first example of heavy fermion superconductivity in a noncentrosymmetric crystal structure. A number of noncentrosymmetric superconductors are known that are not heavy fermion materials, and in fact one of them is the isostructural analog of CePt_3Si , LaPt_3Si with $T_c = 1.0$ K, raising the question as to the

	Ce (4f ¹)	U (5f ³)			Np (5f ⁴)			Pu (5f ⁵)
3d	Co sc $T_c = 2.3 \text{ K}$	Fe pp	Co pp	Ni iafm $T_N = 86 \text{ K}$	Fe iafm $T_{N1} = 118 \text{ K}$ $T_{N2} = 77 \text{ K}$	Co iafm $T_N = 47 \text{ K}$	Ni iafm $T_{N1} = 30 \text{ K}$ $T_{N2} = 30 \text{ K}$	Co sc $T_c = 18 \text{ K}$
4d	Rh sc + lafm $T_N = 3.8 \text{ K}$	Ru pp	Rh pp	Pd iafm $T_N = 30 \text{ K}$	Ru	Rh iafm $T_{N1} = 30 \text{ K}$ $T_{N2} = 32 \text{ K}$	Pd	Rh sc $T_c = 8 \text{ K}$
5d	Ir sc $T_c = 0.4 \text{ K}$	Os pp	Ir pp	Pt iafm $T_N = 26 \text{ K}$	Os	Ir	Pt iafm	Ir pp

sc : Superconductor
 pp : Pauli paramagnet
 lafm : Localized antiferromagnet
 ifam : Itinerant antiferromagnet

Figure 3.30 Ground state of 115 compounds CeTIn_5 and ATGa_5 , where T is a transition metal and A is U, Np, or Pu.

importance of the interplay of noncentrosymmetric crystal structure and heavy fermion character in this superconductivity.

➤ 6. FERROMAGNETIC SUPERCONDUCTORS

We have seen earlier that ferromagnetism in materials such as ErRh_4B_4 caused the reentrance of a normal state at temperatures below the ferromagnetic Curie temperature. Various theoretical arguments suggested, however, that in some cases ferromagnetic order might be compatible with superconductivity with superconductivity occurring near the quantum critical point at which the ferromagnetic Curie temperature is manipulated to approach $T=0$ K. A search was undertaken to explore this possibility, resulting in the discovery of two U-based intermetallics where this was found, UGe_2 [46] and isostructural URhGe [47].

The first successful study came from Lonzarich and collaborators on UGe_2 , following an unsuccessful search for superconductivity under pressure in MnSi . The low-temperature pressure/temperature phase diagram for this orthorhombic compound is shown in Fig. 3.31. UGe_2 is an itinerant ferromagnetic with a Curie temperature of 53 K at ambient pressure. The rather modest pressure of 1.6 GPa is sufficient to drive the Curie temperature to 0 K. What is interesting is that the superconductivity shows up inside the ferromagnetic state near where the Curie temperature vanishes under

Figure 3.31 Superconducting (SC) and ferromagnetic (FM) order in the pressure/temperature phase diagram of UGe_2 [47]. The temperature scale of the superconducting dome is expanded by a factor of 10.

Figure 3.32 Superconductivity (SC) and ferromagnetism (FM) in the low-temperature pressure/temperature phase diagram of URhGe [47]. The temperature scale of region of coexistence of superconductivity with ferromagnetism is expanded by a factor 20.

applied pressure and does not extend beyond the ferromagnetic boundary at 1.6 GPa.

In the subsequently studied isostructural compound URhGe, superconductivity was found to coexist below 0.25 K with small ordered moment ($0.4 \mu_B$) ferromagnetism with Curie temperature 9.6 K. The suggestion here for establishing a congruence between the behavior of URhGe and UGe_2 is that URhGe is at ambient pressure close to its magnetic quantum critical point. A comparison of the properties of URhGe at ambient pressure and UGe_2 at 1.5 GPa makes this argument reasonable. The effect of pressure (Fig. 3.32) on URhGe is opposite to that of UGe_2 with the Curie temperature increasing with applied pressure. We note that the electronic specific heat coefficients of UGe_2 and URhGe are 120 and 160 mJ/mol K², respectively, in the lower heavy fermion range. This is still a relatively unexplored area of the magnetic/superconducting boundary and awaits further experiment.

REFERENCES

- [1] Matthias BT, Suhl H, Corenzwit E. Phys Rev Lett 1958;1:92.
- [2] Abrikosov AA, Gor'kov LP. JETP 1961;12:1243.

- [3] Maple MB, Hamaker HC, Woolf LD. In: Fischer Ø, Maple MB, editors. Topics in current physics, vol. 34. Berlin, Heidelberg, New York: Springer; 1982. p. 99.
- [4] Ginzberg VL. Sov Phys JETP 1957;4:153.
- [5] Fischer Ø, Treyvaud A, Chevrel R, Sergent M. Solid State Commun 1975;17:721; Shelton RN, McCallum RW, Adrian H. Phys Lett 1976;56A:213.
- [6] Matthias BT, Corenzwit E, Vanderberg JM, Barz H. PNAS 1977;74:1334.
- [7] Matthias BT, Marezio M, Corenzwit E, Cooper AS, Barz HE. Science 1972;175:1465.
- [8] Fischer Ø, Maple MB. In: Fischer Ø, Maple MB, editors. Topics in current physics, vol. 32. Berlin, Heidelberg, New York: Springer; 1982. p. 12.
- [9] Gupta LC. Adv Phys 2006;55:1460.
- [10] Sugawara T, Euguchi H. J Phys Soc Jpn 1966;21:7258.
- [11] Kondo J. Prog Theoret Phys (Kyoto) 1964;32:37.
- [12] Friedel J. Philos Mag 1954;7(Suppl.):446.
- [13] Anderson PW. Phys Rev 1961;124:41.
- [14] Schrieffer JR, Wolff PW. Phys Rev 1966;194:491.
- [15] Wilson KG. Collective properties of physical systems. In: Lundqvist B, Lundqvist S, editors. Proceedings of the 24th nobel symposium. New York: Academic Press; 1973.
- [16] Fisk Z, Matthias BT, Corenzwit E. PNAS 1969;64:1151.
- [17] Maple MB, Wittig J, Kim KS. Phys Rev Lett 1969;23:1375.
- [18] Andres K, Graebner JE, Ott HR. Phys Rev Lett 1975;35:1779.
- [19] Stewart GR. Rev Mod Phys 1984;56:755.
- [20] Steglich F, Aarts J, Bredl CD, Lieke W, Meschede D, Franz W, et al. Phys Rev Lett 1979;43:1892.
- [21] Ott HR, Rudigier H, Fisk Z, Smith JL. Phys Rev Lett 1983;50:1595.
- [22] Bucher E, Maita JP, Hull GW, Fulton RC, Cooper AS. Phys Rev B 1973;11:440.
- [23] Fisk Z, Ott HR, Smith JL, Mag J. Mag Mater 1985;47&48:12.
- [24] Smith JL, Fisk Z, Willis JO, Ott HR, Lambert SE, Dalichouch Y, et al. J Mag Mag Mater 1987;63&64:464.
- [25] Ott HR, Rudigier H, Fisk Z, Smith JL. Phys Rev B 1985;31:1651.
- [26] Ott HR, Fisk Z. In: Freeman AJ, Lander GH, editors. Handbook on the physics and chemistry of actinides 5. Amsterdam: Elsevier; 1987. p. 85.
- [27] Stewart GR, Fisk Z, Willis JO, Smith JL. Phys Rev Lett 1984;52:679.
- [28] Fisher RA, Kim S, Woodfield BF, Phillips NE, Taillefer L, Hasselbach K, et al. Phys Rev Lett 1989;62:1411.
- [29] Adenwalla S, Lin SW, Zhao Z, Ran QZ, Ketterson JB, Sauls JA, et al. Phys Rev Lett 1990;65:2298.
- [30] Flouquet J. On the heavy fermion road. In: Halperin WP, editor. Progress in low temperature physics, vol. 15, Elsevier; 2005, p. 139.
- [31] Geibel C, Theis S, Kaczorowski D, Mehner A, Grauel A, Seidel B, et al. Z Physik B 1991;83:305.
- [32] Geibel C, Schank C, Theis S, Kitazawa H, Bredl CD, Böhm A, et al. Z Physik 1994;84:1.
- [33] Doniach S. Physica B 1977;91:231.
- [34] Movshovich R, Graf T, Mandrus D, Thompson JD, Smith JL, Fisk Z. Phys Rev B 1996;53:8241.
- [35] Mathur ND, Grosche FM, Julian SR, Walker IR, Freye DM, Haselwimmer RKW, et al. Nature 1998;394:39.
- [36] Hegger H, Petrovic C, Moshopoulou EG, Hundley MF, Sarrao JL, Fisk Z, et al. Phys Rev Lett 2000;84:4986; Petrovic C, Movshovich R, Jaime M, Pagliuso PG, Hundley MF, Sarrao JL, et al. Europhys Lett 2001;53:354; Petrovic C, Pagliuso PG, Hundley MF, Movshovich R, Sarrao JL, Thompson JD, et al. J Phys: Condens Matter 2001;13: L337.

- [37] Pagliuso PG, Petrovic C, Movshovich R, Hall D, Hundley MF, Sarrao JL, et al. *Phys Rev B* 2001;64:100503.
- [38] Park T, Graf MJ, Boulaevskii L, Sarrao JL, Thompson JD. *PNAS* 2008;105:6825.
- [39] Onuki Y, Settai R, Shishido H, Kubo T, Yasuda Y, Betsuyaku K, et al. *J Alloys Compd* 2006;408–412:27.
- [40] Pham LD, Park T, Maquilon S, Thompson JD, Fisk Z. *Phys Rev Lett* 2006;97:056404.
- [41] Fulde P, Ferrel RA. *Phys Rev A* 1964;135:550; Larkin AI, Ovchinnikov YN, *Sov Phys JETP* 1965;20:762.
- [42] Bianchi A, Movshovich R, Oeschler N, Gegenwart P, Steglich F, Thompson JD, et al. *Phys Rev Lett* 2002;89:137002.
- [43] Sarrao JL, Morales LA, Thompson JD, Scott BL, Stewart GR, Wastin F, et al. *Nature* 2002;420:297; Wastin F, Boulet P, Rebizant J, Colineau E, Lander GH. *J Phys: Condens Matter* 2003;15:S2279.
- [44] Aoki D, Haga Y, Matsuda TD, Tateiwa N, Ikeda S, Homma Y, et al. *J Phys Soc Jpn* 2007;76:063701.
- [45] Bauer E, Hilscher G, Michor H, Paul Ch., Scheidt EW, Griбанov A, et al. *Phys Rev Lett* 2004;92:027003.
- [46] Saxena SS, Agarwal P, Ahilan K, Grosche FM, Haselwimmer RKW, Steiner MJ, et al. *Nature* 2000;406:587.
- [47] Aoki D, Huxley A, Ressouche E, Braithwaite D, Flouquet J, Brison J.-P., et al. *Nature* 2001;413:613.