10 Heavy Fermion Superconductivity

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10.1 Overview

When the BCS theory appeared in 1957, Bernd Matthias felt it did not do everything. He thought that it worked for the $p$-electron superconductors such as lead and tin, but the transition metal superconductors such as niobium and vanadium were still unexplained. Aside from his instinct, it was that here the isotope effect was all over the map. This led him to uranium, where his student Hunter Hill did the isotope effect for uranium and found that the orthorhombic $\alpha$–phase had a backward mass squared dependence and that the cubic $\gamma$–phase looked BCS-like. This was Hunter’s thesis work,
and the experiment was difficult enough that those who did not like the result could ignore it. Bernd was also drawn to the U$_6$X superconducting compound with X = Mn, Co, Fe, and Ni. In these compounds, the $T_c$ scaled with the moments, that is, they followed the Slater–Pauling curve. These were the first superconductors discovered that formed with 3$d$ magnetic elements. These early interesting problems in superconductivity were simply hints of what was to come and what would be called highly correlated electron (heavy fermion) behavior.

The heavy–fermion ground state arises at low temperature. Near room temperature, these metals have magnetic moments whose magnetic susceptibility suggest that they would order antiferromagnetically at low temperature. However somewhere below 50 K, unexpected behavior shows up. The electrical resistivity is high for a metal, and the magnetic ordering does not occur. The heat capacity below 10 K is quite large and seems consistent with the presence of magnetic moments. However, when some compounds became superconducting with the heat capacity indicating that the large value was due to the superconducting electrons instead of the magnetic moments, it seemed wrong. It was as if the rocks in a stream bed began to flow instead of the water. There is still no accepted explanation for such behavior.

In 1975 Bucher et al. noted that the compound UBe$_{13}$ had become superconducting with a somewhat large critical field [1]. They said it was likely that pure uranium filaments were present in the sample, and the superconductivity was hence an impurity effect. In 1978, Franz et al. reported in a footnote that the compound CeCu$_2$Si$_2$ had become superconducting [2], but in this case there was not a simple explanation for an impurity effect. In both cases the authors were clearly wondering what had happened but knew it could not be correct. Steglich continued to pursue the superconductivity and in 1979 reported that it was genuine [3]. As a superconducting material, it seemed ordinary except for the heat capacity that was about a thousand times too large. Steglich coined the name of heavy–fermion superconductor by associating the huge heat capacity with a huge mass for the conduction electrons, which was the only parameter that could be adjusted. So there was a superconductor with a heat capacity for the superconducting electrons that was as large as that usually associated with fixed magnetic moments. People who were paying attention considered it an oddity, and little happened.

In 1983 Ott et al. rechecked Bucher’s result and found UBe$_{13}$ to have properties remarkably similar to those of CeCu$_2$Si$_2$ [4]. Polycrystalline and single–crystalline samples were made at Los Alamos and seen to be superconducting. Heat–capacity measurements at Zürich showed that indeed a huge heat capacity was in the superconducting electrons. The condensed–matter physics community began to take notice, and measurements of many other properties began in earnest on both compounds. It was noticed that the temperature dependence of the heat capacity in the superconducting state was not an exponential, as seen in known superconductors and as predicted by
the Bardeen Cooper Schrieffer theory, but rather it was a power law. This suggested that a gap had not opened everywhere on the Fermi surface (Ott et al. 1984) [5]. This is similar to the pairing in superfluid $^3$He, which is non–$s$–wave pairing. This was the first possible example of an exotic superconductor, one in which the Cooper pairs have a symmetry that is not isotropic or almost so. Some theorists sharpened their pencils, and the people in Los Alamos and Zürich were wondering about the analogy to $^3$He because the smoking gun for low–symmetry superconductors would be more than one superconducting phase.

Then in 1984, Stewart et al. reported that UPt$_3$ was superconducting and was another candidate for a low–symmetry superconductor [6]. They had been studying it as a spin–fluctuating material when it went superconducting at low temperatures. While UBe$_{13}$ and CeCu$_2$Si$_2$ were not good Fermi liquid metals (later to become its own field as non–Fermi liquid materials), UPt$_3$ fit the many–body models of Fermi liquids perfectly. The theorists began work and had much success at describing this ground state. However, how the state occurred was and is the mystery of heavy–fermion superconductors.

Also in 1984, Smith et al. began putting impurities into UBe$_{13}$ and found a strange non–monotonic depression of the superconducting transition temperature with the addition of thorium [7]. In 1985, heat–capacity measurements in Zürich showed two huge superconducting transitions, and the analogy to $^3$He and the proof of low–symmetry superconductivity was made [8]. The first material, CeCu$_2$Si$_2$, remained an $s$–wave superconductor. So by 1986, all of the measurements that anyone could think of were being performed around the world, and review articles were being printed such as Fisk et al. 1986 [9] and Fisk et al. 1988 [10]. These also cover non–superconducting heavy–fermion systems that became identifiable once the properties of the superconductors were well known. Many theses were being written, and the old men of superconductivity were thanking the younger experimentalists for breathing new life into superconductivity. Order seemed to be at hand.

Then late in 1986, Bednorz and Müller published their work on high–temperature superconductivity [11], and an avalanche cut a huge swath through condensed–matter physics leaving many subjects deserted. As it developed that high–temperature superconductors were also non–$s$–wave, theorists were well prepared. Only two example of transitions between superconducting states have been found in oxides (Movshovich et al. 1998 [12] and Mota et al. 1999 [13]), and these results are not widely known or accepted. However, all of the modern techniques that came from the original scanning tunnelling microscope have, in the 1990’s, permitted workers to directly measure the symmetry of the superconducting energy gap.

The compound UPt$_3$ had one more surprise left. In 1989, Fisher et al. discovered a second bump in the heat capacity of the superconducting transition [14]. Workers all over the world took the old samples out of their drawers to remeasure this because all had missed it, and it was confirmed to
have two superconducting phases. It was soon seen that the magnetic-field- and-temperature phase diagram had three superconducting phases, and the theoretical description of them was under control quickly.

Now, we have heavy-fermion superconductors and high-temperature superconductors both without an accepted model for how these ground states occur. New theory is still needed. One recent development is the possibility of quantum critical points at zero temperature that hold some promise of explaining the general phase diagrams for both of these superconductors, which usually have an antiferromagnetic state in them. There is a feeling that some larger theoretical picture may emerge and show us all new physics. It is also true that in Germany and Japan, there are now major experimental institutes engaged in the search for more heavy-fermion materials with the usual name now of highly-correlated electron systems. And of course, theoretical work is underway everywhere.

10.2 Introduction

The first heavy-fermion superconductor CeCu$_2$Si$_2$ was discovered by Steglich et al. [3] in 1979. Despite intense skepticism from members of the scientific community, Steglich demonstrated that stoichiometric CeCu$_2$Si$_2$ underwent a transition to a superconducting state at the critical temperature $T_c = 0.7$ K. This material was regarded as a unique anomaly until several other materials were discovered which had the same distinctive normal state properties. Some of these heavy-fermion materials [4, 6] even have similar unusual superconducting phases. This class of heavy-fermion materials can be loosely categorized as systems that are in close proximity to a magnetic instability, and have the characteristic properties that at high temperatures, the system exhibits evidence of local moments; at low temperatures, the system resembles a Fermi liquid with very heavy quasi-particle masses. The heavy-fermion materials are based on elements from the lanthanide or actinide series which have incomplete $f$ shells. The $f$ derived electronic states retain a lot of their ionic character in that they are almost localized and experience large electronic interactions attributable to the smallness of the radius of the ionic $f$ orbitals. The heavy-fermion materials are those in which there is a delicate balance between the strong ionic coulomb interactions that tend to localize the electrons and yield local magnetic moments, and the hybridization with extended band states that tends to delocalize the $f$ electrons. The delicate balance is responsible for the temperature dependent cross-over from the high temperature local moment regime to the low temperature regime of itinerant $f$ electron behavior. At high temperatures, the magnetic moments are manifested via the Curie-Weiss variation of the magnetic susceptibility with Curie constants almost equal the full ionic magnetic moments, and also through a Kondo-like logarithmic temperature variation of the electrical resistivity indicating resonant scattering of conduction electrons from independent lo-
cal moments. In the low temperature regime, the strong electron–electron interactions show up as strong renormalizations of the properties of the itinerant electrons. The excitations of the interacting electron gas include quasi–particle excitations that closely resemble the excitations of a non–interacting electron gas. The quasi–particles have dispersion relations that form narrow correlated $f$ bands close to the Fermi energy. The quasi–particle masses, as inferred from the coefficient, $\gamma$, of the low temperature linear $T$ term of the specific heat, can be as large as 1000 free electron masses. The masses of the heavy quasi–particle are assumed to have evolved from the entropy released during the transformation of the high temperature magnetic moments. The specific heat coefficient $\gamma$ determined from the normal state of CeCu$_2$Si$_2$ is roughly 1100 mJ/mole K$^2$, while that of the paramagnetic heavy–fermion CeCu$_6$ [15] system is 1300 mJ/mole K$^2$. The low temperature susceptibilities $\chi(T)$ are also enhanced above the values of the Pauli paramagnetic susceptibilities inferred from the density of states obtained via LDA calculations. The values of the low temperature susceptibilities can be as large as $28 \times 10^{-3}$ e.m.u./mole for CeCu$_6$ and $16 \times 10^{-3}$ e.m.u./mole for CeRu$_2$Si$_2$ [16]. A measure of the relative strengths of enhancements experienced by the susceptibility and the specific heat is given by the Wilson ratio,

$$R_W = \frac{\pi^2 k_B^2 \chi(0)}{3\mu_B^2 \gamma}$$

(10.1)

which has the ideal value of unity for the non–interacting electron gas. However, the values of the Wilson ratio found for most heavy–fermion systems are also close to unity. Comparison of the $\gamma$ values and the low temperature limit of the magnetic susceptibilities with the densities of states at the Fermi energy found in LDA electronic structure calculations [17] indicate that the quasi–particle masses are enhanced by factors as large as 25, presumably due to strong electron–electron interactions. This interpretation is supported by the observation of a $T^3 \ln T$ term in the specific heat of UPt$_3$, which is characteristic of spin–fluctuations driven by strong electron–electron interactions. In addition, the low temperature electrical resistivities of some materials, such as CeCu$_6$, show $\rho(T) = \rho(0) + A T^2$ variations where the coefficient $A$ takes on large values. The large value of $A$ is indicative of the formation of a Fermi liquid state in which the resistivity is dominated by scattering between the heavy quasi–particles. In this interpretation, the value of $A$ is a measure of the inverse square of the renormalized Fermi energy. The most direct and definitive evidence proving the existence of the heavy Fermi liquid state is given by the measurement of de Haas–van Alphen oscillations [18, 19]. In a number of materials, large quasi–particle mass enhancements have been found over significant portions of the Fermi surface. The large quasi–particle masses inferred for some or all portions of the Fermi surface correlate well with the measured value of $\gamma$. Evidence of the strong magnetic correlations is provided by the fact that, in many heavy–fermion systems, the addition of small amounts of impurities allows the strong electron interactions to drive
the system magnetic. This suggests that the heavy–fermion systems may be in the vicinity of a quantum critical point and that the extremely large mass enhancements are produced by the nearly critical magnetic fluctuations. Unlike the U heavy–fermion systems, the Ce systems seem to show properties that are attributable to strongly localized fluctuating magnetic moments, so that a large part of the mass enhancement for the Ce heavy–fermion compounds may result from the local moment fluctuations.

Large mass enhancements can also be inferred from the normal state specific heats of the uranium heavy–fermion superconductors UBe$_{13}$ [4], UPt$_3$ [6] and URu$_2$Si$_2$ [20, 21], which have magnitudes that are of the same order as in the heavy–fermion Ce compounds. The observed $\gamma$ values are 1100 mJ/mole K$^2$ for UBe$_{13}$, 400 for UPt$_3$, and 60 mJ/mole K$^2$ for URu$_2$Si$_2$. The magnetic susceptibilities $\chi$, in the low temperature normal state, are also enhanced. For UBe$_{13}$, which has a cubic structure, the low temperature normal state susceptibility has a value of $14 \times 10^{-3}$ e.m.u./mole. In UPt$_3$, which has hexagonal symmetry, the susceptibility is anisotropic, having the value of $4 \times 10^{-3}$ e.m.u./mole for fields along the c–axis and $8.1 \times 10^{-3}$ in the basal plane. In URu$_2$Si$_2$, which has tetragonal symmetry, the susceptibility is $4.9 \times 10^{-3}$ for fields along the c–axis and $1.5 \times 10^{-3}$ e.m.u./mole in the perpendicular directions. Fermi liquid analyses of the specific heat and susceptibility are complicated by the existence of unusual low temperature magnetic phases and correlations. In fact, while the large values of the $\chi$ and $\gamma$ may be considered as indicative of the formation of a highly enhanced Fermi liquid, the resistivity of UBe$_{13}$ is still large $\sim$ 100$\mu$Ω cm, and although rapidly varying, it shows no evidence of a $T^2$ variation setting in before the superconducting transition occurs $^1$. The large magnitude of the specific heat jump that occurs at the superconducting transition temperature, $T_c$, shows that the electrons that take part in the formation of the heavy–fermion state form the Cooper pairs. That is, the normalized jump discontinuity $(C_s - C_n) / C_n$ is of the order of unity, similar to the B.C.S value of 1.43, which indicates that the superconducting electrons have heavy masses (see Fig. 10.1). A similar conclusion is arrived at by a thermodynamic analysis of the extremely large initial slopes of the upper critical fields $(\partial H_{c2}/\partial T)_{T_c}$ [22–24] which is about $-42$ T/K for UBe$_{13}$.

The equilibrium superconducting state is that which minimizes the total energy, including the strong Coulomb interaction between the f electrons that gives rise to the enhanced masses in the Ce and U heavy–fermion materials. The superconducting electrons could form Cooper pairs with finite angular momentum, $l$, which could lower the Coulomb repulsion between the pairing electrons as the pair wave function vanishes at the origin. The decrease in the large Coulomb energy could offset the increase in kinetic energy due to the orbital motion. The finite angular momentum of the pairs could also lead to

$^1$ However, when magnetic fields large enough to suppress the superconductivity are applied, UBe$_{13}$ does exhibit a $T^2$ term in the resistivity.
the superconducting gap at the Fermi energy falling to zero at either isolated points or lines, giving rise to a finite density of states for low-energy quasi-particle excitations. These point zeros and line zeros give rise to power law variations with $T$ for various physical properties, which are in contrast to the exponentially activated behavior usually observed in $s$–wave superconductors. Such power law variations have been found in experiments [5,25–31] and show conclusive evidence of low-energy excitations. However, the observed power laws have not led to a consensus as to whether they are caused by either point zeros or line zeros in the order parameter. This lack of consensus could be due to the complications of either pair breaking effects of impurities in anisotropic superconductors or due to collective fluctuations. In either case, heavy–fermion superconductors are examples of exotic superconductors.

10.2.1 Multiple Superconducting Phases

Soon after the discovery of the uranium heavy–fermion superconductors [4], it was noticed that some heavy–fermion superconductors exhibited multiple
superconducting phases. This discovery gave strong support to the hypothesis that the superconductivity involved exotic pairings. Motivated by the discovery of the power law temperature variations and the implications about the zeros in the gap, Smith et al. [7] doped the superconductors with impurities to find their effect on the superconducting transition temperature $T_c$, as it is well known that non–magnetic impurities suppress anisotropic pairing. It was found that substitution of just a few percent of Th atoms on the U sites in UBe$_{13}$ produced a large non–monotonic change in $T_c$ and also reduced the value of the resistivity at constant $T$ [7]. Measurements of the specific heat [8] showed a spectacular result namely, that for Th concentrations in the range $0.01 < x < 0.06$, the specific heat shows two jumps that have comparable discontinuities (see Fig. 10.2). The upper transition is associated with a large Meissner effect and has a maximum $T_{c1}$ near 0.6 K in this range of $x$, whereas the second transition occurs at $T_{c2}$, which is approximately 0.4 K. The existence of the second transition in the doped samples was confirmed by sound velocity and ultrasonic attenuation experiments [32]. The sound velocity showed a pronounced minimum at $T_{c2}$, while the attenuation showed a peak. The second superconducting phase was assigned as having some intrinsic weak magnetic character. The magnetic nature of the second transition was later confirmed via improved muon spin resonance measurements [33], which show that weak magnetic moments of the order $10^{-3} \mu_B$ are formed below $T_{c2}$ but only in the concentration range $0.01 < x < 0.06$. The phase diagram is shown in Fig. 10.3. The existence of two superconducting phases,
Fig. 10.3. A $T - x$ phase diagram for $U_{1-x}Th_xBe_{13}$. Filled symbols denote phase transitions and open symbols indicate anomalies in the specific heat (C) and thermal expansion ($\alpha$). The solid vertical line at $x = x_1$ represents a phase boundary established by the specific heat measurements under pressure of Zieve et al. [501]. [After Oeschler et al. (2003), [497]]

in analogy with the phase diagram of $^3$He, is further evidence of the unconventional nature of the superconducting order parameter. If the system were an $s$–wave superconductor and the Fermi surface were isotropically gapped at $T_{c1}$, it seems very unlikely that the large jump in the specific heat at $T_{c2}$ would be due to a weak magnetic transition that merely coexists with the superconducting transition. If the superconducting gap is anisotropic having nodes, the electronic states in the vicinity of nodes could take part in a magnetic transition and could result in the small size of the moments [34]. However, it still remains unlikely that magnetic ordering of these states could produce a large jump in the specific heat. An alternate possibility is that the second transition is between two distinct unconventional superconducting phases, one of which may involve broken time reversal symmetry [35]. This alternate possibility was given credence by the measurements performed by
Fig. 10.4. The lower critical field $H_{c1}$ of $U_{1-x}Th_xBe_{13}$ for $x = 0.03$, as measured by Rauchschwalbe et al. (1987) [36]. The temperature of the kink indicates the existence of a second transition.

Rauchschwalbe et al. [36] where $H_{c1}(T)$ showed a quadratic $T$ dependence with a coefficient that abruptly changes at $T_{c2}$ (see Fig. 10.4). This suggests that the lower transition is between two superconducting phases that have different types of order parameters. The faster temperature variation of $H_{c1}$ below $T_{c2}$ is interpretable as due to an increase in the superconducting condensation energy.

Careful measurements on $UPt_3$ also revealed the presence of two jumps in the specific heat [14] with critical temperatures separated by 60 mK. The specific heat jumps for two different samples of $UPt_3$ are shown in Fig. 10.5. The application of a magnetic field in the basal plane reduces both transition temperatures [37], but the 60 mK splitting observed at $H = 0$ is diminished and the transitions merge at a critical point ($H_{c2}(T) = 5$ kOe and $T = 380$ mK). The $H - T$ phase diagram of $UPt_3$ is shown in Fig. 10.6. A definite kink in the temperature derivative of $H_{c2}(T)$ had been previously observed at this field [38, 39]. The splitting between the two jumps in the specific heat depends on the direction of the applied field. Application of a field parallel to the $c$ direction does not reduce the splitting between the transitions, and for this field direction, the critical field does not show any discontinuity in the slope of $H_{c2}(T)$ up to the highest measured fields (7.5 kOe). The lower critical field, $H_{c1}(T)$, has a similar dependence on the orientation of the field [40]. A sharp kink in the temperature dependence of $H_{c1}$ was observed for fields in the basal plane, and no kink was found for fields parallel to the $c$-axis. Evidence for further structure in the $H-T$ phase diagram was provided by
Fig. 10.5. The double transition in the specific heat found in two samples UPt$_3$ found by Fisher et al. (1989) [14]

ultrasonic attenuation measurements. Early on, Qian et al. [41] and Müller et al. [42] observed a $\lambda$ anomaly in the ultrasonic attenuation, just below $T_c$ for longitudinal waves at H= 0. The position of the attenuation peak splits at higher fields, and the peak continues deep within the superconducting state as a cusp-like feature. Initially, the attenuation experiments were given scant attention by the scientific community, but given the preponderance of evidence for multiple superconducting phases, ultrasonic measurements are now recognized as providing excellent evidence for a phase boundary between different superconducting phases [43]. For H fields in the basal plane, this phase boundary appears to join up with the phase boundaries obtained from the two specific heat jumps at the very point where the splitting between the jumps disappears. The complete phase diagram of UPt$_3$ has been obtained from anomalies in the measured velocity of acoustic phonons [44, 45]. The phase diagram in the $H - T$ plane shows the existence of five superconducting phases in contrast to the two usually observed in type II superconductors. The phase diagram contains two distinct Meissner phases in addition to three
Fig. 10.6. The temperature–field phase diagram of UPt$_3$, as deduced from sound-velocity measurements of Adenwalla et al. (1990) [44]. The applied field is in the basal plane. The inset shows the phase diagram when the applied field is directed along the $c$ axis. The low field boundary separating the mixed and the Meissner phases is not shown.

mixed phases seen in Fig(10.6). These phases of superconducting UPt$_3$ are discussed in more detail on page 1056. The transition to the superconducting phase of UPt$_3$, at zero field and ambient pressure, occurs at a temperature of 0.5 K, which is well below the Néel temperature of $T_N \sim 6K$ at which a small moment antiferromagnetic phase occurs. The application of uniaxial or hydro-static pressure shows that the splitting between the zero field superconducting transitions disappears above a critical pressure [46, 48, 49]. As shown in Fig. 10.7, the pressure at which the two jumps in the specific heat merge coincides with the pressure where the antiferromagnetism also disappears [46]. This suggests that the appearance of multiple superconducting phases in UPt$_3$ is intimately related to the occurrence of magnetic ordering.

10.2.2 Interplay of Superconductivity and Magnetism

A further notable characteristic of the heavy-fermion superconductors is that, with the exception of UBe$_{13}$, UGe$_2$, and URhGe, the superconducting phases coexist with antiferromagnetic correlations which have characteristic temperatures, usually $T_N$, that can be roughly an order of magnitude greater than the corresponding superconducting critical temperatures. The strengths of
Fig. 10.7. The integrated intensity of the magnetic peaks \((\frac{1}{2}, 1, 0)\) and \((\frac{1}{2}, 0, 1)\) of UPt\(_3\) at \(T = 1.8\) K as a function of hydrostatic pressure \([46]\) is shown in (a). The magnetic Bragg peak intensity should correspond to the square of the order parameter. The Néel temperature \(T_N\), as determined from the integrated intensities, is shown as a function of pressure in (b). The critical pressure at which the magnetism disappears coincides with the pressure at which the specific heat jumps merge \([47]\).

The antiferromagnetic correlations are weakest for the systems that show the largest mass enhancements, such as CeCu\(_2\)Si\(_2\), UPt\(_3\) and U\(_{1-x}\)Th\(_x\)Be\(_{13}\), where the size of the moments is at most minute, of the order of 0.03 \(\mu_B\). Muon spin resonance experiments on these three materials indicate that magnetic fluctuations have extremely long characteristic time scales. On the other hand, the more recently discovered compounds URu\(_2\)Si\(_2\), UNi\(_2\)Al\(_3\) \([50]\) and UPd\(_2\)Al\(_3\) \([51]\) have much smaller \(\gamma\) coefficients which, if estimated above the respective Néel temperatures, are only as large as 150 mJ / mole K\(^2\). The \(\gamma\) values below the Néel temperatures are reduced, indicating a partial gapping of the Fermi surface. These moderately enhanced materials have \(T_N\)'s that can be as high as 14.5 K and have ordered magnetic moments that range up to 0.85 \(\mu_B\).
Fig. 10.8. The pressure–temperature phase diagram of the ferromagnetic superconductor UGe$_2$ [66]. The Curie temperature were determined from the susceptibility (filled circles), resistivity (open circles) and neutron diffraction (squares). The onset and completion of the resistive superconducting transition are shown by the filled triangles. Note the change of scale for the superconducting transition temperature.

For a long time, CeCu$_2$Si$_2$ was the only known Ce based heavy–fermion superconductor at ambient pressure. However, this compound suffered from materials problems namely, a small change in stoichiometry could result in the ground state changing from superconducting to antiferromagnetic. Very recently it was found that CeIrIn$_5$ and CeCoIn$_5$ superconduct at $T_c = 0.4$ and $T_c = 2.3$ K, respectively [52,53]. Furthermore, these materials are almost always single crystals and apparently do not suffer from the same problems as exhibited by CeCu$_2$Si$_2$. These new heavy–fermion superconductors have a quasi–two–dimensional structure. They are quite anisotropic and exhibit well defined crystal field excitations at high temperatures [54] and at low temperatures show de Haas – van Alphen oscillations characteristic of anisotropic Fermi surfaces [55,56]. More important, they show that the superconductivity occurs in the vicinity of magnetism [57]. The quasi–two–dimensional nature of the materials and the anisotropy of the magnetically ordered states is favorable for the existence of large amplitude magnetic fluctuations in the superconducting state. In the superconducting state, the specific heat, thermal conductivities [59,60] and NMR $1/T_1$ relaxation rates [61,62] show the power law temperature variations, which are consistent with the superconducting order parameter having lines of nodes. Since these materials share many common features with cubic CeIn$_3$, which is also antiferromagnetic and superconducts ($T_c \approx 200$ mK) at pressures greater than 25 kbar [63], together
they form a family of materials in which the effect of structure (such as the role of dimensionality or magnetic anisotropy) on the interplay of superconductivity and magnetism can be investigated.

Since it was a commonly held belief that ferromagnetism is detrimental to superconductivity, it was a great surprise when superconductivity was discovered in the ferromagnetic phase of UGe$_2$ [65]. As shown in Fig. 10.8, the superconducting phase in UGe$_2$ occurs for pressures in the range of 1 to 1.5 GPa [66] where the material is ferromagnetically ordered. As the pressure is increased from 1 to 1.5 GPa, the critical temperature for ferromagnetic ordering shows indications of rapidly decreasing from about 30K to 0, while the maximum superconducting transition temperature is only 0.7K and falls to zero at a pressure where the ferromagnetism disappears. URhGe which goes superconducting at ambient pressure for temperatures below 0.25K, also has a ferromagnetic Curie temperature $T_c = 9.5$K which is unusually small [67]. Since uniform internal magnetic fields are pair breaking for the singlet–pairs of a BCS superconductor, it has been suggested that in these systems the Cooper pairs are in a triplet state. However, if this is the case, there seems
to be no compelling reason as to why the superconducting phase should be restricted to only occur inside the ferromagnetic phase. On the other hand, if the ferromagnetic state can be described strictly as a local Fermi liquid [69], then it has been rigorously shown [70] that there is an attractive s-wave interaction and the triplet interaction is identically zero. Furthermore, a mean field analysis shows that a singlet superconducting state in a ferromagnet may survive if the pair breaking due to the uniform internal field is sufficiently strong [71].

The observation of the superconducting phase within ferromagnetic and antiferromagnetic phases with low transition temperatures shows that the heavy–fermion materials are often correlated with the proximity of a quantum critical point [72–74]. This point is illustrated by the phase diagrams shown in Figs. 10.8 through 10.10. At a quantum critical point, the large amplitude low frequency magnetic fluctuations could produce appreciable contributions to physical properties that are different from those expected of highly renormalized quasi–particles. The existence of large amplitude magnetic fluctuations associated with the quantum critical point leads to another exciting possibility namely, that the superconducting pairing mechanism for the quasi–particles is primarily mediated by low–energy spin–fluctuations [75]. Either the characteristic frequency of the low–energy spin–fluctuations or the mass renormalizations associated with the heavy quasi–particles presumably, could be responsible for setting the low values of the superconducting transition temperatures, \( T_c \). Generally, heavy–fermion superconductors have superconducting transition temperatures in the range between 0.2 and 3 K. The compound PuCoGa5 provides a notable exception to this statement, as it has a \( T_c \) of about 18.5 K, which is the highest reported \( T_c \) for a heavy–fermion.
superconductor [76]. The low values of $T_c$ found in most heavy–fermion superconductors are in stark contrast with the very large critical temperatures found in the other well known examples of exotic superconductivity – the high temperature superconducting cuprates.

10.2.3 Quasi–Particles and Collective Excitations

At high temperatures, the properties of heavy–fermion systems can often be described in terms of a set of local moments coupled to a sea of conduction electrons. At temperatures below a characteristic temperature, sometimes known as the coherence temperature, the properties show evidence that the excitations have large spatial extents. Below the coherence temperature, the transport properties indicate that the scattering from the spin degrees of freedom start to freeze out and that the electronic excitations extend throughout the crystal. For sufficiently low temperatures, one may expect that the properties will be described by the quasi–particle excitations of Landau Fermi liquid theory. However, in a few of the heavy–fermion systems, the Fermi liquid state is never completely formed before superconductivity sets in. In these cases one expects that, below the coherence temperature, the properties may be determined by the low–energy excitations that include both the collective excitations, such as phonons and spin–waves, as well as the quasi–particle excitations.

Quasi–Particle Excitations

Elementary excitations can be categorized either as quasi–particles or as collective excitations. The quasi–particle excitations are in one–to–one correspondence with the excitations of the non–interacting system. The quasi–particle excitations have a close similarity to the single–electron excitations of a non–interacting electron gas. The properties of these quasi–particles are most readily seen through inspection of the one–electron thermal Green’s function [77] defined by the expectation value of the time ordered product of the thermal average

$$G^{\alpha,\beta}_{\mathbf{k},\mathbf{k}'}(\tau) = -\frac{1}{\hbar} < \hat{T}_{\mathbf{k},\alpha} a_{\mathbf{k}',\beta}(\tau) a^\dagger_{\mathbf{k},\alpha}(0) > .$$

(10.2)

The Green’s function represents the time evolution of the probability amplitude for a single electron to be added to the Bloch state with wave vector $\mathbf{k}$ and spin $\sigma$. The electron creation and annihilation operators are evaluated in the imaginary time representation where they evolve according to the prescription

$$a_{\mathbf{k},\sigma}(\tau) = \exp\left[ -\frac{\hat{H}}{\hbar} \tau \right] a_{\mathbf{k},\sigma}(0) \exp\left[ +\frac{\hat{H}}{\hbar} \tau \right].$$

(10.3)

Due to periodic translational invariance and spin rotational invariance of the normal state, the Green’s function is diagonal in the wave vector and spin
The Fourier transform of the diagonal Green’s function is defined via

\[ G(k; \tau) = k_B T \sum_n G(k; i\hbar \omega_n) \exp \left[ -i \omega_n \tau \right], \tag{10.5} \]

where

\[ \hbar \omega_n = k_B T \pi (2n + 1), \tag{10.6} \]

are the Matsubara frequencies. The interacting Green’s function is expressed in terms of the non–interacting Green’s function \( G^0(k; i\hbar \omega_n) \) and the self–energy \( \Sigma(k; i\hbar \omega_n) \) through Dyson’s equation

\[ \left[ G(k; i\hbar \omega_n) \right]^{-1} = \left[ G^0(k; i\hbar \omega_n) \right]^{-1} - \Sigma(k; i\hbar \omega_n), \tag{10.7} \]

where the non–interacting Green’s function is evaluated as

\[ \left[ G^0(k; i\hbar \omega_n) \right]^{-1} = i \hbar \omega_n - e(k) + \mu. \tag{10.8} \]

The pole of the non–interacting Green’s function is at the single–electron Bloch energy \( e(k) - \mu \), and measures the excitation energy relative to the Fermi energy. The self–energy represents the change in the Green’s function due to the interactions. The Fermi energy of the interacting system, \( \mu \), is determined by the pole of the Green’s function at \( \omega_n = 0 \), which leads to

\[ \mu = e(k_F) + \Sigma(k_F; 0), \tag{10.9} \]

where \( k_F \) is a Bloch vector on the Fermi surface. The thermal Green’s function is related to the \( T = 0 \) Green’s function via analytic continuation \( i \hbar \omega_n \to E \). The correspondence between quasi–particle excitations and the single–electron excitations of the non–interacting system follows from the expansion of the self–energy near the Fermi energy. For energies close to the Fermi energy, the Green’s function can be re–written as

\[ \left[ G(k; E) \right]^{-1} \approx E \left( 1 - \frac{\partial \Sigma(k; E)}{\partial E} \right) \bigg|_{\omega=0} - e(k) - \Sigma(k; 0) + \mu - i \text{Im} \Sigma(k; E) \]

\[ = \left( 1 - \frac{\partial \Sigma(k; E)}{\partial E} \right) \bigg|_{\omega=0} \left[ E - E_k + \frac{i \hbar}{2} \tau_k(E) \right]. \tag{10.10} \]
The interaction produces a linear superposition of the electron in a Bloch state $\mathbf{k}$ with one–electron states surrounded by a cloud of electron–hole pairs. The quasi–particle weight, $Z_k^{-1}$, represents the fraction of this superposition that corresponds to the bare Bloch electron. The fraction is less than unity $Z_k > 1$, and $Z_k$ is given in terms of the frequency derivative of the self–energy by

$$Z_k = 1 - \left. \frac{\partial \Sigma(k; E)}{\partial E} \right|_{E=0} .$$

(10.11)

The quasi–particle energy $E_k$, measured from the Fermi energy $\mu$, and the decay rate are given by

$$E_k = e(k) + \Sigma(k; E_k) - \mu ,$$

$$E_k \approx Z_k^{-1} \left( e(k) + \Sigma(k; 0) - \mu \right) ,$$

(10.12)

and

$$\frac{\hbar}{2\tau_k^*(E)} = - Z_k^{-1} \text{Im} \Sigma(k; E + i\delta)$$

(10.13)

respectively. Since the imaginary part of the Green’s function is proportional to the single–particle density of states, the self–energy can be viewed as a renormalization of the single–electron excitation energies $e(k)$, yielding the quasi–particle energy $E_k$. The imaginary part of the self–energy can be viewed as providing the width or lifetime of the single–particle state. As shown by Luttinger [78], the imaginary part of the self–energy near the Fermi energy due to electron–electron interactions vanishes proportional to $E^2$, if perturbation theory converges. The small magnitude of the lifetime is due to the Pauli exclusion principle which reduces the phase space allowed for electron–electron scattering. The smallness of the lifetime of low–energy excitations has the effect that the spectrum resembles that of a non–interacting electron gas in which the quasi–particle masses are enhanced by a factor of $Z_k$. The quasi–particle states are extremely long lived, not only because of the vanishing of the lifetime due to electron–electron interactions but also because the residual lifetime resulting from elastic scattering by impurities is enhanced by the factor of $Z_k$. Due to the extremely small magnitude of the lifetime of quasi–particles at the Fermi energy, the Fermi energy is well defined and the effect of electron–electron interactions does not change the volume enclosed by the Fermi surface [78]. It is found that, in de Haas – van Alphen experiments on some of the heavy–fermion systems, the multi–sheeted Fermi surfaces enclose volumes that are consistent with Luttinger’s theorem being valid. For heavy–fermion systems, the $k$ dependence of the self–energy is considered to be small, and the frequency dependence is extremely rapid. Thus,
the quasi–particles are expected to be extremely heavy and long–lived but have little spectral weight. Also, a large portion of the weight is expected to lie in the broad incoherent portion of the spectral density.

Since the quasi–particles are governed by Fermi–Dirac statistics, their contributions to thermodynamic quantities have asymptotic low temperature variations that are similar to those of the non–interacting electron gas. In particular, the entropy $S$ of the gas of quasi–particles is given by

$$S = -k_B \sum_{\sigma, \delta} \left[ (1 - f(E_\delta)) \ln[1 - f(E_\delta)] + f(E_\delta) \ln[f(E_\delta)] \right]. \quad (10.14)$$

Hence, the quasi–particles give rise to a linear $T$ contribution in the low temperature electronic specific heat. However, the coefficient $\gamma$, instead of just reflecting the electronic density of states, is given by the density of quasi–particle energies at the Fermi surface

$$\rho_{qp}(E) = \sum_k \delta(E - E_k),$$

$$\rho_{qp}(0) \sim \sum_k Z_k \delta(\mu - e(k) + \Sigma(k;0)), \quad (10.15)$$

which is enhanced over the electronic density of states $\rho(\mu)$ by a factor $Z$ similar to the Fermi surface average of $Z_k$. Comparison of the low temperature electronic specific heat coefficient $\gamma$ and electronic structure calculations, yields an estimate of the wave function renormalization $Z$ of approximately 25 for highly enhanced systems such as UPt$_3$. The heavy quasi–particle masses in some or all parts of the Fermi surface can also be inferred from the amplitude of the de Haas – van Alphen oscillations in the magnetization [79]. The signatures of the gas of heavy quasi–particles may also be expected to show up in transport properties, albeit modified by the residual interactions between the quasi–particles. The temperature dependence of the d.c. resistivity of the enhanced Fermi liquid state is dominated by the transport scattering rate. If the self–energy is roughly $k$ independent, the transport scattering rate should coincide with the scattering rate $\frac{1}{\tau}$ found from the imaginary part of the self–energy since the conductivity vertex corrections are expected to be small. For low temperatures and samples of high purity, Matheissen's rule is expected to apply. In this case, the scattering rate is additive, and $\frac{1}{\tau}$ is expected to be composed of a sum of a temperature independent term $\frac{1}{\tau_0}$ due to the potential scattering from isolated impurities, a quadratic Baber term caused by the quasi–particles scattering off of each other, and a negligibly small $T^5$ term expected from electron–phonon scattering

$$\frac{1}{\tau} = \frac{1}{\tau_0} + A T^2 + B T^5. \quad (10.16)$$

If the impurity scattering can be treated in the Born approximation, then, due to the approximate invariance of the density of states at the Fermi energy,
the impurity scattering rate $\frac{1}{\tau_0}$ is not directly renormalized by the electron–electron interactions. The $T^2$ Baber term has its origin in the Pauli–exclusion principle limiting the phase space available for scattering of low–energy electrons, and is exactly the same physics behind the $E^2$ variation of the imaginary part of the self–energy. Since Baber scattering involves the scattering of two quasi–particles, the scattering rate is enhanced by a factor proportional to $Z^2$. The residual d.c. conductivity does not directly depend on the real part of the self–energy and is, therefore, un–renormalized. Alternately, the d.c. residual resistivity is un–renormalized due to the small magnitude of the velocity vertex correction, and due to the cancellation of the wave function renormalization in the ratio of the renormalized quantities

$$\frac{\tau^*}{m^*} \approx \frac{\tau}{m} \quad (10.17)$$

and also because the electron density $n$ is unchanged by electron–electron interactions. This last fact is seen by noting that $n$ is proportional to the Fermi surface volume which, according to Luttinger’s theorem, is independent of the strength of electron–electron interactions. Despite the absence of significant renormalization of the d.c. conductivity, the renormalized lifetimes do show up as extremely narrow widths of the Drude peak [80–82]

$$\text{Re} \left[ \sigma(\omega) \right] = \frac{n \, e^2 \, \tau^*}{m^*} \, \frac{1}{1 + \omega^2 \, \tau^*^2} \quad (10.18)$$

observed in measurements of the dynamical conductivity $\sigma(\omega)$ at low temperatures. The frequency dependence of the measured conductivity $\sigma(\omega)$ for UPt$_3$ [80], is shown in Fig. 10.11 for low and high temperatures. Basically, if one has a fixed concentration of impurities, and hence a fixed mean free path, then the quasi–particle lifetime is just determined by the quasi–particle velocity $\hbar \, k_F / m^*$, which is reduced by the large quasi–particle mass. Therefore, the enhanced effective mass results in an enhancement of the lifetime due to impurity scattering. At higher frequencies, one expects that inelastic scattering processes should become important and the quasi–particle weight should acquire a frequency dependence. The frequency dependence of the scattering rate and the quasi–particle renormalization are expected to be related by causality and other requirements. In particular, the optical sum rule [83] relates the integral of the optical conductivity over all frequencies to the total number of electrons in the system

$$\int_0^\infty d\omega \text{Re} \left[ \sigma(\omega) \right] = \frac{\pi}{2} \frac{n \, e^2}{m_e} \quad (10.19)$$

where $n$ is the density of electrons and $m_e$ is the electron mass. Similarly, the integrated intensity of the low frequency Drude peak

$$\int_0^{\omega_0} d\omega \text{Re} \left[ \sigma(\omega) \right] = \frac{\pi}{2} \frac{n(\omega_0) \, e^2}{m^*} \quad (10.20)$$
Fig. 10.11. The optical conductivity $\sigma(\omega)$ of single crystals and polycrystals of UPt$_3$ at $T = 1.2$ K and $T = 20$ K [80]. The data show the growth of the narrow quasi–particle Drude peak at low temperatures.

can be used to define the number of coherent quasi–particles $n(\omega_0)$ and their weight $Z^{-1}$ [84], whereas the higher energy structure is due to the incoherent excitations. The existence of the quasi–particle Drude peak has been confirmed in UPt$_3$, CeAl$_3$ and CeCoIn$_5$ [80, 81, 85], however, it has not been observed in UBe$_{13}$ [86] where it is doubtful that a Fermi liquid is formed at temperatures higher than the superconducting $T_c$. In the cases where the Fermi liquid is fully formed, it is not expected that good agreement will be found between the optical effective mass, whose definition involves the Fermi surface average of the inverse quasi–particle mass, and the Fermi surface average quasi–particle mass obtained from specific heat. The disagreement is expected to be marked specially if the de Haas – van Alphen experiments show both light and heavy quasi–particle excitations co–existing on the Fermi surface.

In systems like UBe$_{13}$, the Fermi liquid phase is not completely formed before superconductivity sets in, therefore, the thermodynamic and transport properties may be directly affected by the collective excitations of the electrons. In addition, the large mass renormalization $Z$ of the quasi–particles might also be attributable to the existence of low frequency collective excitations, such as local spin–fluctuations or more extended magnetic excitations that are precursors of long–ranged magnetic ordering. The collective excitations are directly amenable to experimental observation and also may mediate residual interactions between the quasi–particles, and therefore, they could be responsible for the superconducting pairing.
Collective Excitations
Since the normal states of heavy-fermion materials are characterized by a large quasi-particle density of states near the Fermi-level, they are susceptible to entropy-driven instabilities, which reduce the density of states at the Fermi energy. This tendency is manifested by the sensitivity of the normal state to small amounts of added impurities that can lead to an instability towards states with spontaneously broken symmetries. If the interactions are short-ranged and the symmetry that is broken is continuous, Goldstone’s theorem [87] is valid. Goldstone’s theorem ensures that the system will support a branch of collective excitations with a zero threshold energy that dynamically restores the spontaneously broken symmetry. The order parameter acts as the collective coordinate for the zero energy collective excitations. The spin-waves with $q \approx 0$ in a ferromagnet, the antiferromagnetic spin-waves near the critical wave vector(s) $Q_c$, and the transverse sound waves in a periodic solid, form well known examples of these Goldstone collective modes. Similar boson-like collective excitations are expected to occur in the disordered or high temperature state as precursors to the instabilities. In the disordered state, these boson modes are expected to have extremely long lifetimes and have excitation spectra that form broad continua. A well known example of these precursor modes is provided by the paramagnon fluctuations in Pd, which occur as Pd is very close to an instability to a ferromagnetic state [88–90]. It is expected that, as the temperature is lowered through the instability, these pre-critical modes will merge together with the critical fluctuations and, eventually, the (Goldstone) spin-wave modes will emerge in the ordered state. There is a growing body of evidence that suggests that heavy-fermion systems are in the vicinity of a quantum critical point, implying that the system supports large amplitude critical fluctuations due to a nearby $T = 0$ phase transition. One expects that the properties of the material should show scaling behavior due to the quantum critical point. The critical fluctuations near a quantum critical point are expected to have a different nature than those associated with a finite temperature transition as they cannot be treated classically [72–74]. The zero-point quantum fluctuations replace the role of the thermally-driven fluctuations. Since the dynamics are inextricably linked to the statics at a quantum critical point, the phase space of the magnetic fluctuations is given by $(\omega, \mathbf{k})$. If the characteristic frequency scales as $\xi^{-z}$, where $\xi$ is the magnetic correlation length and $z$ is the dynamical exponent, then the effective dimensionality of the phase space for a $T = 0$ quantum critical point is given by $d_{\text{eff}} = d + z$. Hence, as the effective dimensionality $d_{\text{eff}}$ differs from the dimensionality $d$ of the classical critical point, one expects to find different types of scaling relations at a quantum critical point. The search for the ultimate description of quantum critical fluctuations is an actively ongoing field of research.

The simplest starting point for these theories of the collective spin-fluctuation modes lies in the Random Phase Approximation (RPA) [91,92]. The
RPA is the crudest approximation that captures the physics of the Gaussian fluctuations and is most certainly expected to fail near the quantum critical point. In most approaches, one assumes that the Coulomb interaction is highly screened, and this results in a Hubbard point contact interaction $U$ between electrons of opposite spins. Within the quasi–particle treatment, the band energies $e(k)$ should be replaced by the quasi–particle energies $E_k$, and the interaction should be expressed in terms of the Landau Fermi–liquid parameters. However, we shall, in the rest of this section, be consistent with the usual formulation of RPA as a one parameter Fermi liquid, in which the interaction between the quasi–particles is denoted by $U$. Since we shall neglect the vertex corrections to the susceptibility, we shall also suppress all the factors of $Z^{-1}$, while it is true that Fermi liquid corrections should renormalize $U$ to $U/Z^2$. Although the results are derived on the basis of a one band Hubbard model, they can easily be extended to a two band or Anderson Lattice model [93]. The transverse susceptibilities are expressed in terms of multiple scattering processes involving an up–spin electron with a down–spin hole shown in Fig. 10.12 [91, 92], yielding

$$\chi^-(q,\omega) = \mu_B^2 \chi_0(q,\omega) \left( \frac{1}{1 - U \chi_0(q,\omega)} \right),$$

where $\chi_0(q,\omega)$ is the non–interacting Lindhard susceptibility, given by

$$\chi_0(q,\omega) = \frac{1}{N} \sum_k \left[ \frac{f(e(k)) - f(e(k + q))}{\hbar \omega - e(k) + e(k + q) + i \delta} \right].$$

In the RPA, a magnetic instability of the paramagnetic state towards an ordered state with ordering wave vector $Q$ is obtained when the static susceptibility $\chi(Q,0)$ diverges, which occurs due to the vanishing of a denominator. This happens when the generalized Stoner criterion is fulfilled,

$$1 = U \chi_0(Q,0),$$

where $\chi_0(Q,0)$ is the reduced non–interacting susceptibility. The paramagnetic state is unstable for values of $U$ greater than a critical value $U_c$ where
the equality of (10.23) first holds, at any value of $Q$. The type of instability, determined by $Q$ and the critical value of $U$ at which it occurs, is governed by both the quasi–particle band structure and the state of occupation of the bands. If $\chi_0(Q;0)$ is largest at $Q = 0$, the system is expected to become unstable to a ferromagnetic state at a critical value of $U$ determined by the usual Stoner criterion for ferromagnetism, $1 = U_c \rho(\mu)$. For perfect nesting tight–binding bands at half filling, one finds that $\chi(Q;0)$ diverges for $Q = \pi (1,1,1)$, leading to an instability towards an antiferromagnetic state for $U$ greater than the critical value of $U_c = 0$ [94]. In general, for $U$ values close to the critical value $U_c$, the static susceptibility evaluated at the relevant $Q$ is enhanced, and the imaginary part of the susceptibility undergoes a similar enhancement. Since the imaginary part of the susceptibility is a measure of the spectrum of magnetic excitations, the enhanced RPA expressions

$$
\text{Im} \left[ \chi^{+-}(q;\omega) \right] = \frac{\mu_B^2 \text{Im} \chi_0^{+-}(q;\omega)}{\left[ 1 - U \text{Re} \chi_0^{+-}(q;\omega) \right]^2 + \left[ U \text{Im} \chi_0^{+-}(q;\omega) \right]^2} \tag{10.24}
$$

show the propensity for low frequency large amplitude spin–fluctuation excitations, as shown in Fig. 10.13. Near the instability, the magnetic excitation spectrum consists of a continuum of low–energy (quasi–elastic) and over–damped precritical fluctuations from which, on increasing $U$ above $U_c$, a branch of sharp spin–wave excitations are expected to emerge in the magnetically ordered state.

The large amplitude spin–fluctuations are also expected to give rise to a renormalization of the quasi–particles. The change in the energies of the
Fig. 10.14. The RPA expression for the up–spin electron self–energy $\Sigma(k;E)$. The one–electron Green’s function is denoted by the directed line, and the spin–fluctuation by a wavy line. In this process, an up–spin electron of momentum $k$ emits a spin–fluctuation of momentum $q$, thereby flipping its spin.

quasi–particles shows up in the RPA self–energy due to the emission and absorption of spin–waves, which flip the spin of the electron (see Fig. 10.14). The quasi–particle weight of the low frequency excitations is reduced as the scattering from the large amplitude spin–fluctuations reduces the probability that the electron remains in a spatially extended Bloch state. For a nearly ferromagnetic system, this leads to a logarithmic enhancement of the linear term in specific heat [89,90] via

$$C \propto k_B T \ln \left| 1 - U \rho(\mu) \right|. \quad (10.25)$$

Using a Fermi liquid approach, Carneiro and Pethick [95] have shown that long wavelength collective fluctuations can also lead to a $T^3 \ln T$ term in the specific heat similar to that found in paramagnon theories [96]. Likewise, the collective fluctuations also can lead to an enhancement of the quasi–particle scattering rate which in turn, leads to an enhanced $T^2$ term in the electrical resistivity [88,97]. The precise form of the renormalization found in RPA does depend crucially on the type of magnetic instability (ferromagnetic, incommensurate spin density wave, antiferromagnetic) that is being approached. For example, in quantum phase transitions with finite ordering wave vectors $Q$, electrons are resonantly scattered by magnetic fluctuations between portions of the Fermi surface that are connected by the vector $Q$ (see Fig. 10.15). This leads to the occurrence of hot lines on the Fermi surface where the quasi–particles are extremely short lived and, therefore, are not well–defined. The size of these hot regions is proportional to $\sqrt{T}$. On the other hand, for a ferromagnetic quantum critical point, the entire Fermi surface is subject to critical scattering. The different nature of the critical scattering results in different power law temperature dependences of various physical quantities [98]. For example, the leading non–analytic part of the free energy $\Delta F$ is given by
Fig. 10.15. Hot lines on a Fermi surface. The dynamic susceptibility becomes critical at wave vector $Q$. The electrons on the two lines of the Fermi surface which are connected by wave vector $Q$ are subject to resonant scattering. The width of the hot lines is given by $\xi^{-1}$, which is proportional to $\sqrt{T}$.

$$\Delta F = \sum \int_0^\infty \frac{d\omega}{\pi} \left[ N(\omega) + \frac{1}{2} \right] Im \left[ \ln U \chi(q;\omega) \right],$$  (10.26)

where $N(\omega)$ is the Bose–Einstein distribution function, and the spin–fluctuation propagator either has the form

$$\chi(q;\omega)^{-1} \sim (1 - I) + a \left( \frac{q}{k_F} \right)^2 + i b \left( \frac{\hbar \omega k_F}{\mu q} \right)$$  (10.27)

near a ferromagnetic instability or has the form

$$\chi(q;\omega)^{-1} \sim (1 - I) + a \left( \frac{q - Q}{k_F^2} \right)^2 + i b \left( \frac{\hbar \omega}{\mu} \right)$$  (10.28)

near an antiferromagnetic instability. For a $d$ dimensional system that is above the critical dimensionality, at a quantum critical point where $I = 1$, this produces a leading $T^{1+d/3}$ temperature dependence of $\Delta F$ for a ferromagnetic quantum critical point, but near an antiferromagnetic quantum critical point $\Delta F$ has a $T^{1+d/2}$ dependence. The temperature dependence of $\Delta F$ gives rise to the non–analytic temperature dependences of the $C/T$ ratio.

Close to a quantum critical point, where both thermal and quantum critical fluctuations are important, the properties are expected to be significantly different from the properties calculated using simple RPA. At finite temperatures and in the quantum critical region, the effect of coupling among the different modes of spin–fluctuations becomes important [99]. The theories of Moriya [92], Hertz [72] and Millis [74] predict that three dimensional electronic systems at a quantum critical point have an effective dimensionality greater than the upper critical dimension and, hence, are dominated by Gaussian spin–fluctuations, albeit highly renormalized by mode–mode coupling. In
this case, the hyperscaling relation is not expected to be obeyed. The strength of the mode–mode coupling is expected to vanish at zero temperature. It is generally believed that the region over which the Fermi liquid behavior is found, is smaller for systems which are close to exhibiting a magnetic instability. Furthermore, as the quantum critical point is approached, the Fermi liquid power laws are expected to be gradually replaced by other types of non–universal power laws. For example, the $T^2$ variation of the resistivity found in the Fermi liquid regime of a clean three–dimensional metal is expected to be replaced by a $T^3$ variation at a ferromagnetic quantum critical point or a $T^2$ variation at an antiferromagnetic quantum critical point. These power laws are intermediate between the low temperature Fermi liquid $T^2$ variation and the linear $T$ variation found within RPA at higher temperatures and are consistent with expectations based on the shrinking temperature range over which Fermi liquid behavior is to be observed. The simple power laws obtained using self–consistent spin–wave theory are only expected to be recovered at low temperatures. Furthermore, the scaling behavior expected from the quantum critical point is expected to be severely modified by the effects of disorder [100, 101]. In the case of an antiferromagnetic quantum critical point in a clean system, the hot lines are not expected to dominate drastically the low temperature physical properties, since the hot lines have a limited extent. For example, the contributions of the hot lines to the conductivity are expected to be shorted out by the normal regions of the Fermi surface [102]. However, the presence of impurities leads to $k$ not being a good quantum number since electrons are inelastically scattered between different portions of the Fermi surface. Hence, the mixing between different $k$ values results in all the electrons on the Fermi surface participating in the critical scattering [101].

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<th>Table 10.1. Quantum critical exponents for physical properties.</th>
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<td>$d = 3$</td>
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<td>$C/T$</td>
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In general, the power laws found in heavy–fermion systems do not coincide with those found in the above–mentioned type of two or three dimensional theories (shown in Table(10.1).). One possible cause for this discrepancy is
perhaps due to the heaviness of the quasi–particle masses. That is, in the above theories, the electron dynamics are assumed to occur on a fast energy scale compared with the slow critical fluctuations, therefore the fast electron dynamics can be integrated out. For systems with high effective masses, such descriptions may no longer be appropriate [103]. Related ideas about the lack of scaling being caused by the breakdown of the quasi–particle concept have been expressed by Coleman [104]. An alternate possible cause for the discrepancy could be due to the nature of the assumed theoretical model 2. Generally, it has been assumed that strong electron–electron interactions, which give rise to the formation of heavy quasi–particles and strong magnetic fluctuations, are unfavorable for the formation of superconducting pairs. However, the observation of superconducting phases only in the immediate vicinity of quantum critical points, as sketched in Fig. 10.16, challenges the assumption. These observations suggest that the large amplitude quantum critical fluctuations might even be responsible for the occurrence of the superconductivity. The two most outstanding questions about the superconductivity in heavy–fermion systems concern the nature of the pairing mechanism and the symmetry of the superconducting order parameter.

2 The Moriya, Hertz, Millis theory assumes the validity of a non–degenerate one–band model, whereas multi–band models, with orbital degeneracy and strong spin–orbit coupling, appear to be more appropriate for describing heavy–fermion systems. These other models may be in a different universality class and, hence, have other critical exponents.
10.2.4 Possible Pairing Mechanisms

The interaction mechanism that is responsible for pairing electrons in common superconductors is mediated by phonons. Fröhlich [105] predicted that the superconducting transition temperature $T_c$ should be proportional to a typical phonon frequency. Furthermore, as the phonon frequency squared is inversely proportional to the mass of the ions, $M$, Fröhlich predicted that the transition temperature should vary as

$$T_c \propto M^{-\frac{1}{2}}.$$ \hspace{1cm} (10.29)

This dependence of $T_c$ on the mass was confirmed by experiments by Maxwell [106] and Reynolds et al. [107] who measured $T_c$ for samples composed of different isotopes. This isotope effect has been observed in a number of simple materials such as Hg, Pb, Mg, Sn, Tl. For these simple metals, the retarded electron–electron attraction, due to the charged ions over screening the Coulomb interaction [108], has a simple mass dependence. The isotope effect is much smaller or even almost absent in transition metals and compounds such as Ru and Os, where the electrons are more localized and the relative strength of the Coulomb repulsion is large [109]. In $\alpha-U$, a large isotope effect even occurs with a positive exponent [110], but detailed calculations show that the superconductivity is still phonon mediated [111]. The absence of an isotope effect does not necessarily imply non–phonon mediated electron–electron interactions but merely that simplifying circumstances that lead to Fröhlich’s isotopic mass dependence are not present. As heavy–fermion systems have extremely heavy quasi–particle masses due to large electron–electron interactions, one does not expect isotope experiments to provide direct evidence of the nature of the pairing mechanism. Furthermore, for systems that appear to be on the verge of a magnetic instability [112, 113], it is possible that the collective excitations of the spin system could provide an alternate or complementary mechanism to the phonon mediated interaction.

Many different pairing mechanisms have been proposed for heavy–fermion superconductors, ranging from electron–phonon coupling [114, 115] to ferromagnetic and antiferromagnetic spin–fluctuations [116–118]. The main problem posed in developing a microscopic description of the superconductivity lies with the lack of knowledge of the normal state because of its strong electron correlations. A commonly used approach that describes the formation of the superconducting state starts from assuming the validity of a Fermi liquid description of the normal state. In what follows, we shall outline this approach to superconductivity. However, as some heavy–fermion superconductors show no evidence that a Fermi liquid state has formed before the superconducting transition has occurred, this approach is not on a firm basis. Second, as the Fermi liquid approach neglects the effect of the collective fluctuations, it does not address the role that the low–frequency spin–fluctuations play in suppressing the superconducting transition. The proper starting point for a microscopic description of electron–phonon mediated superconductivity lies
The directed double lines represent the fully renormalized Green’s function in the Eliashberg equations \[119, 120\] in which the superconducting gap, or order parameter, is related to a time varying quantity \( \Sigma^{(a)}(\mathbf{k}; \tau) \), which is the anomalous or pair self–energy in the superconducting state. The gap parameter in the quasi–particle spectra, \( \Delta_{\alpha,\beta}(\mathbf{k}; i\hbar\omega_n) \), is defined in terms of the anomalous self–energy and wave function renormalization via

\[
\Delta(\mathbf{k}; \omega_n) = \frac{\Sigma^{(a)}(\mathbf{k}; i\hbar\omega_n)}{Z_{\mathbf{k}}(i\hbar\omega_n)}.
\]

(10.30)

The self–energy \( \Sigma^{(a)}_{\alpha,\beta}(\mathbf{k}; i\hbar\omega_n) \) is depicted diagrammatically in Fig. 10.17. A rigorous derivation of the Eliashberg equations for the self energies relies on the validity of Migdal’s theorem \[121\], which states that the vertex correction is tiny, of the order of the square root of the ratio of the electron to the ion mass \( \sim 10^{-3} \). There are no analogous theorems known for couplings to other bosonic modes such as spin–waves \[122\], but nevertheless, it is still hoped that similar equations may describe superconducting pairing mediated by other bosonic mechanisms. In the Eliashberg equations, the gap can be expressed in terms of the spectral density associated with the bosonic pairing mechanism and the spectral density of the electrons forming the Cooper pairs. In the presence of strong interactions, the spectral densities include appropriate self energies, and the pairing interaction is manifested through an irreducible vertex interaction, \( \Gamma(\mathbf{k}, \mathbf{k} + \mathbf{q}; i\hbar\omega_m, i\hbar\omega_n)_{\alpha,\beta;\mu,\nu} \). Terms corresponding to the irreducible vertex interaction due to the exchange of bosons are shown in Fig. 10.18. The self–energy, the gap, and the irreducible vertex interaction should all be calculated self consistently. The linearized gap equation, which
The normal state becomes unstable to the superconducting state that has the highest $T_c$ in the case of no degeneracy. The criterion for a further instability of superconducting phase to phases with other types of pairings must be determined on the basis of minimization of the free energy. In the case of strong electron–phonon coupling, the vertex corrections are limited by Migdal’s theorem \[121\] to be smaller than the bare vertex interaction by factors at least as small as $10^{-2}$. These corrections are negligibly small and, therefore, have the effect that the self–energies can be calculated with extremely good accuracy. In such cases, the Eliashberg equations have been solved. Such calculations are reviewed in references \[123, 124\]. For heavy–fermion superconductors, the physics is not so clear and, despite the absence of experimental confirmation, the validity of a Fermi liquid picture is often assumed. Under this assumption, the imaginary time Green’s functions in the vicinity of the Fermi energy may be replaced by their quasi–particle contributions. In particular, the quasi–particle masses are changed from the band mass $m_b$ by the wave function renormalization to $Z m_b$, the quasi–particle lifetimes $\tau_0$ are increased to $Z \tau_0$ and the strength of the quasi–particle pole is reduced from unity by a factor $Z^{-1}$. The enhanced quasi–particle masses are simply absorbed into a re–definition of $e(k) - \mu$ as the normal state quasi–particle energies $E_k$. If the electron–phonon coupling was proven to be the mechanism responsible for heavy–fermion superconductivity, the ratio of the quasi–particle masses to the ionic masses are no longer negligible so, even in this case, Migdal’s theorem and the Eliashberg equations may be of doubtful validity. Even though retardation plays an important role in superconductivity, an approximation that has been frequently used consists of replacing the vertex function by an appropriate interaction potential evaluated on the Fermi surface. In this case, the Feynman diagram expansion of the irreducible vertex interaction $\Gamma(q; \hbar \omega)$ in terms of bosonic excitations.

$$
\Delta_{\alpha,\beta}(k; i \hbar \omega_n) = -k_B T_c \frac{1}{N} \sum_{m} \sum_{q} \sum_{\mu,\nu} \Gamma(k, k + q; i \hbar \omega_m, i \hbar \omega_n)_{\alpha,\beta,\mu,\nu} 
\times G_{\mu}(k + q; i \hbar \omega_m) G_{\nu}(-k - q; -i \hbar \omega_m) \Delta_{\mu,\nu}(k + q; i \hbar \omega_m).
$$

(10.31)
approximation, the interaction potential contains the effect of the instantaneous Coulomb repulsion, and the linearized gap equation simplifies to take the weak-coupling BCS form [125],

\[
\Delta_{\alpha,\beta}(\mathbf{k}) = Z^{-2} \frac{1}{N} \sum_{\mathbf{q}} \sum_{\mu,\nu} \Gamma(\mathbf{k},\mathbf{k}+\mathbf{q})_{\alpha,\beta,\mu,\nu} \Delta_{\mu,\nu}(\mathbf{k}+\mathbf{q}) \times \left[ \frac{1 - f(E_{\nu,\mathbf{k}+\mathbf{q}}) - f(E_{\mu,\mathbf{k}-\mathbf{q}})}{E_{\nu,\mathbf{k}+\mathbf{q}} + E_{\mu,\mathbf{k}-\mathbf{q}}} \right].
\]  

(10.32)

This differs from the usual BCS theory of simple superconductors in that the wave function renormalization \(Z^{-1}\) is now explicitly included, and also, there is an implicit difference in that the dispersion relations are those of the heavy quasi-particles. The spin dependence of the quasi-particle energies may be important for the occurrence of superconductivity within a magnetically ordered phase. The summation over \(\mathbf{q}\) can be performed by introducing an integration over the density of states which is cut off at a frequency \(\omega_c\), characteristic of the bosons responsible for the pairing

\[
\Delta_{\alpha,\beta}(\mathbf{k}) = Z^{-2} \rho(\mu) \sum_{\mu,\nu} \int \frac{d\Omega}{4\pi} \Gamma(\mathbf{k},\mathbf{k}')_{\alpha,\beta,\mu,\nu} \Delta_{\mu,\nu}(\mathbf{k}') \times \\
\times \left[ 1 - 2f(\hbar\omega_c) \right] \ln \frac{\hbar\omega_c}{k_B T} + 2 \int_0^{\frac{\hbar\omega_c}{k_B T}} dx \ln x \frac{\partial}{\partial x} \left( \frac{1}{\exp x + 1} \right) \\
= Z^{-1} \rho(\mu) \sum_{\mu,\nu} \int \frac{d\Omega}{4\pi} \Gamma(\mathbf{k},\mathbf{k}')_{\alpha,\beta,\mu,\nu} \Delta_{\mu,\nu}(\mathbf{k}') \left( 1 - 2f(\hbar\omega_c) \right) \ln \frac{\hbar\omega_c}{k_B T} + \ln \frac{2\gamma}{\pi},
\]

(10.33)

where we have ignored any spin polarization in the quasi-particle bands. Usually, the Fermi function \(f(\hbar\omega_c)\) is neglected under the assumption that \(\hbar\omega_c > k_B T_c\), which usually holds for phonon mediated pairing. However, this assumption may not be appropriate for spin-fluctuation mediated pairing near a quantum critical point. In such cases, a strong coupling approach may have to be used. In the above expression, the electron density of states \(\rho(\mu)\) is un-enhanced by the interactions but is multiplied an explicit factor of \(Z^{-1}\), i.e.,

\[
k_B T_c = 1.14 \hbar\omega_c \exp \left[ - \left( \frac{Z}{\Gamma \rho(\mu)} \right) \right],
\]

(10.34)
where \( \Gamma \) is the Fermi surface average of \( \Gamma(\hat{k}, \hat{k}') \). Thus, the mass renormalization \( Z \) could depress \( T_c \). The value of \( T_c \) in heavy–fermion superconductors could also be low due to a small \( \omega_c \) in the prefactor \([127]\) as well as in the exponent due to the appearance of the Fermi functions.

The relationship between the nature of spin–fluctuations and the singlet or triplet character of the pairing is found by expanding both the on–Fermi surface vertex function and the order parameter in spherical harmonics. The expansions are

\[
\Gamma(\hat{k}, \hat{k}')_{\alpha,\beta;\mu,\nu} = \sum_{l,m} \Gamma(l)_{\alpha,\beta;\mu,\nu} Y^l_m(\hat{k})^* Y^l_m(\hat{k}') 
\]

(10.35)

and

\[
\Delta_{\mu,\nu}(\hat{k}) = \sum_{l,m} \Delta_{\mu,\nu}(l,m) Y^l_m(\hat{k}) .
\]

(10.36)

The orthogonality of the spherical harmonics \( Y^l_m \), leads to an independent linearized gap equation for each \( l \) value. Furthermore, if the spin dependence of the vertex function is of the form

\[
\Gamma(l)_{\alpha,\beta;\mu,\nu} = \left( U_l \delta_{\alpha,\beta;\mu,\nu} - J_l \vec{\sigma}_{\alpha;\mu} \cdot \vec{\sigma}_{\beta;\mu} \right),
\]

(10.37)

where \( U_l \) is an effective direct Coulomb repulsion and \( J_l \) is an effective exchange, then, with the aid of the identity

\[
\left( S(S+1) - \frac{3}{4} \right) \delta_{\alpha,\beta;\mu,\nu} = \frac{1}{2} \vec{\sigma}_{\alpha;\mu} \cdot \vec{\sigma}_{\beta;\mu},
\]

(10.38)

where \( S \) is the total spin of the Cooper pair, one can show that the equations for the different \( T_c \)'s are

\[
1 = \ln \frac{k_B T_c}{\hbar \omega_c} \rho(\mu) \left( U_l + 3 J_l \right) 
\]

(10.39)

for singlet \( T_c \)'s with \( S = 0 \) and even \( l \), while

\[
1 = \ln \frac{k_B T_c}{\hbar \omega_c} \rho(\mu) \left( U_l - J_l \right) 
\]

(10.40)

for triplet \( T_c \)'s with \( S = 1 \) and odd \( l \). The normal state becomes unstable to the angular momentum pairing state with the highest \( T_c \). In the case where a set of order parameters have degenerate \( T_c \)'s, the instability first occurs to the state with the linear combination of the order parameters that corresponds to the lowest free energy \([128,129]\). Large values of \( U_0 \), from the direct Coulomb repulsion, are unfavorable for \( s \)-wave pairing. However, \( U_0 \) represents the residual interactions between a pair of quasi–particles and is represented by a Fermi liquid parameter \( F_0 \) which is unknown, apriori, and it could have a
Fig. 10.19. The RPA expression for the irreducible interaction between a pair of electrons with parallel spins is depicted in terms of Feynmann diagrams in (a). The interaction between electrons with anti-parallel spins is shown in (b). The interaction not only involves the longitudinal spin-fluctuations but also transverse spin-fluctuations.

Quite small magnitude in which case s-wave pairing might still occur. It is also seen that the $q$ dependence of the effective exchange interaction strongly influences the tendency for singlet versus triplet pairing [130, 131].

In analogy to the paramagnetic spin-fluctuation pairing mechanisms [132–134] proposed for $^3$He, a number of authors [116–118] have investigated the effect of incommensurate or antiferromagnetic spin-fluctuations within the RPA. The effective interaction between a pair of electrons with parallel spins is shown in Fig. 10.19a. The dashed lines represent the local Coulomb interaction, and the directed lines represent the one-electron Green’s functions. These diagrams only contain odd numbers of bubbles due to the spin-dependent nature of the Coulomb repulsion $U$ and are related to the longitudinal or z-z components of the magnetic susceptibility. The resulting interaction between parallel spin electrons at the Fermi energy is given by

$$\Gamma(k, k')_{\sigma, \sigma; \sigma, \sigma} = -\frac{U^2 \chi_0(k - k'; 0)}{1 - U^2 \chi_0^2(k - k'; 0)},$$

(10.41)
where \( \chi_0(q; 0) \) is the static limit of the appropriate transverse, non–interacting, reduced susceptibility, having the usual Lindhard form.

The effective interaction between electrons with anti–parallel spins is given by the sum of three terms, one being the on site Coulomb repulsion \( U \), another term stemming from the transverse susceptibility, and the last term originates from the remaining part of the longitudinal susceptibility. These terms are depicted diagrammatically in Fig. 10.19b and are evaluated as

\[
\Gamma(k, k') = U + \frac{U^3 \chi_0^2(k - k'; 0)}{1 - U^2 \chi_0(k - k'; 0)} + \frac{U^2 \chi_0(k + k'; 0)}{1 - U \chi_0(k + k'; 0)}.
\]

For values of \( U \) in the vicinity of the critical value \( U_c \), the susceptibilities for \( q \sim Q \) are enhanced as are the effective quasi–particle interactions of Eqn. (10.41) and Eqn. (10.42). Thus, one expects the effective interaction to be highly peaked at \( q \) values closely connected to the \( Q \) values of the quantum critical point. Due to the increase in the amplitude of the spin–fluctuations as the quantum critical point is approached, the superconducting interaction in the paramagnetic phase is expected to be largest just at the quantum critical point. In the magnetically ordered phase, the transverse spin–fluctuations are expected to transform into a branch of undamped Goldstone modes. However, as shown by Schrieffer \textit{et al}. [135], the Goldstone modes of the antiferromagnetically ordered state of an isotropic material do not produce superconducting pairing. Due to the loss of the low–energy transverse spin–fluctuation modes as a pairing mechanism in the ordered phase and as the amplitude (longitudinal) modes are expected to acquire a mass, one expects that the superconducting pairing will diminish deep within the magnetically ordered phase. Hence, the superconductivity is expected to occur only in close proximity to a quantum critical point.

In comparing the relative tendencies of the nearly ferromagnetic and nearly antiferromagnetic spin–fluctuations in producing triplet or singlet pairings [130, 131], it is useful to re–write the momentum transfers for on–Fermi surface processes as \( | \vec{k} \pm \vec{k}' |^2 = 2k_F^2 (1 \pm \cos \theta) \), where \( \cos \theta = \hat{k} \cdot \hat{k}' \). Then, with the use of the addition theorem for spherical harmonics, one finds

\[
J_l = \frac{2 l + 1}{4} \int_0^\pi d\theta \sin \theta P_l(\cos \theta) \frac{U^2 \chi_0(k - k'; 0)}{1 - U \chi_0(k - k'; 0)},
\]

where \( P_l(x) \) are the Legendre polynomials. If the system is close to a ferromagnetic instability, the effective interaction due to the spin–fluctuations is

\footnote{The combined effect of spin–orbit coupling and crystalline anisotropy in a heavy–fermion system may result in the magnetic order parameter losing its continuous symmetry. Hence, the nature of the soft–modes at the transition may change. In such cases, it might be expected that the soft–modes may remain effective in producing superconducting pairing within the magnetically ordered phase.}
enhanced and positive for momentum transfers of magnitude \( q = 2k_F \sin \frac{\theta}{2} \sim 0 \), and from the properties of the Legendre function, one expects that the strengths of \( J_l \) are positive ( \( P_l(1) = 1 \) ) and decrease with increasing \( l \) due to the increasing number of nodes of \( P_l(\cos \theta) \). This, combined with a large value of \( U_0 \), may forbid \( s \)-wave singlet pairing and leads to the conclusion that ferromagnetism may favor triplet spin pairing with \( l = 1 \). That is, a ferromagnetic exchange between distant electrons can stabilize triplet pairs [136]. On the other hand, if the proximity to a spin density wave phase enhances the susceptibility at non–zero \( q \) values in regions where the odd \( l \) values of \( P_l(\cos \theta) \) are negative ( \( P_l(-1) = (-1)^l \) ), triplet pairing may be unfavorable. However, even \( l \) singlet pairing may still occur as it is stabilized by the antiferromagnetic exchange. Such a simple analysis of the strength of the various pairings is not expected to hold in real materials with multi–sheeted Fermi surfaces but is crucially controlled by the structure of the Fermi surface of the normal state [75].

The usual weak–coupling description of superconducting states, developed by Bardeen Cooper and Schrieffer [125], has a starting point that assumes the normal state electronic system is in the Fermi liquid state. The superconducting pairing interaction is introduced, which then produces the instability to the superconducting state. To the extent that the pairing interactions can be treated in the mean–field approximation, the quasi–particle concept remains valid in the superconducting state. The absence of a significant lifetime for the quasi–particle states essentially follows from the same reasoning as in the normal state, namely, that the Pauli–exclusion principle significantly reduces the amount of phase space available for scattering processes. In this mean–field description, the quasi–particle dispersion relations \( E_{\sigma,k} \) have forms that depend on the nature of the superconducting order parameters. For the majority of conventional superconductors, the normal state is well described by Fermi liquid theory, and the transition to the superconducting state closely follows the mean–field predictions. However, measurements on some heavy–fermion systems show that the systems have not settled into the Fermi liquid phase before the superconducting transition occurs. Thus, the validity of the use of the quasi–particle concept is dubious. Nevertheless, it may be expected that some features of the heavy–fermion superconducting states are robust in that they only depend on underlying symmetries and thus, would be common to the mean–field description in terms of quasi–particles as well as a more rigorous treatment.

10.2.5 The Symmetry of the Order Parameter

The symmetry of the superconducting order parameter, or more precisely the vanishing of the gap at the Fermi energy, does lead to anomalous temperature dependences of specific heat and transport properties far below \( T_c \). An early series of such experiments which were devised to elucidate the symmetry did lead to the conclusion that the superconducting gap does vanish somewhere
on the Fermi surface [5, 25–31] but was equivocal on the detailed nature of the order parameter. Nevertheless, in the following we shall examine the possible symmetries of the gap function and their experimental manifestations. These considerations shall then be applied to the various heavy-fermion compounds in subsequent sections.

The Cooper pairs are characterized by the pairing function, which is defined by the expectation value of the product of two electron annihilation operators, $a_{\sigma, \mathbf{k}}$, as

$$\Phi_{\alpha, \beta}(\mathbf{k}) = \langle a_{\alpha, \mathbf{k}} a_{\beta, -\mathbf{k}} \rangle,$$  \hspace{1cm} (10.44)

where $\alpha$ and $\beta$ denote the spin values quantized along the $z$ axis. We shall consider the equilibrium state in which the center of mass of the pairs are at rest. For convenience we shall, as in the case of superfluid $^3$He [137], assume spherical symmetry and also neglect spin–orbit scattering. Neither of these assumptions are valid for heavy-fermion systems [138]. For $f$ electrons, spin–orbit coupling is known to be strong, and the anisotropy caused by the crystalline environment also needs to be accounted for. So, both these assumptions need to be abandoned in a proper description of heavy-fermion superconductors. As their abandonment only complicates the presentation [139, 140] but does not invalidate the general approach being outlined, we shall make use of these assumptions for pedagogical purposes. This approach mirrors the historical development of the theoretical description of heavy-fermion superconductivity, which often proceeded by analogy with $^3$He.

The singlet pairing function is written as the anti–symmetrized product

$$\Phi^s(\mathbf{k}) = \langle ( a_{\uparrow, \mathbf{k}} a_{\downarrow, -\mathbf{k}} - a_{\downarrow, \mathbf{k}} a_{\uparrow, -\mathbf{k}} ) \rangle.$$  \hspace{1cm} (10.45)

The triplet pairing functions can be expressed in terms of the components organized by the eigenvalues of $S_z$ as

$$\Phi^t_{S_z=1}(\mathbf{k}) = \langle a_{\uparrow, \mathbf{k}} a_{\uparrow, -\mathbf{k}} \rangle,$$

$$\Phi^t_{S_z=0}(\mathbf{k}) = \langle ( a_{\uparrow, \mathbf{k}} a_{\downarrow, -\mathbf{k}} + a_{\downarrow, \mathbf{k}} a_{\uparrow, -\mathbf{k}} ) \rangle,$$

and

$$\Phi^t_{S_z=-1}(\mathbf{k}) = \langle a_{\downarrow, \mathbf{k}} a_{\downarrow, -\mathbf{k}} \rangle.$$  \hspace{1cm} (10.46)

From consideration of the fermion anti–commutation relations, one finds that the singlet pairing function is even in $\mathbf{k}$ whereas the triplet wave function is odd in $\mathbf{k}$. By considering the effects of various symmetries on an arbitrary pairing wave function, one finds that in this case, one can parameterize an arbitrary pairing function in terms of a scalar singlet $\Phi^s(\mathbf{k})$ and a (vector) triplet $\Phi^t(\mathbf{k})$ pairing function via

$$\Phi_{\alpha, \beta}(\mathbf{k}) = \frac{1}{2} \left[ \left( \Phi^s(\mathbf{k}) + \mathbf{\sigma} \cdot \mathbf{\Phi}^t(\mathbf{k}) \right) i \sigma_y \right]_{\alpha, \beta}.$$  \hspace{1cm} (10.47)
The unitary operator \( i \sigma_y \) occurs as a consequence of the spin operator \( \sigma^t \) being odd under time reversal symmetry and also as the anti-symmetric Pauli matrix has the effect that

\[
    i \sigma_y \sigma^t = - \sigma^t.
\]  

The direction of the triplet ordering is given in terms of the matrix elements of the vector pairing function

\[
    \bar{\Phi}^t(k) = \left[ -\Phi^t_{S_z=1}(k) (\hat{x} + i\hat{y}) + \Phi^t_{S_z=0}(k) \hat{z} + \Phi^t_{S_z=-1}(k) (\hat{x} - i\hat{y}) \right].
\]  

If the pairing interaction is of the form

\[
    \hat{H}_{int} = \frac{1}{N} \sum_{k, q} \sum_{\alpha, \beta, \mu, \nu} V(k, q)_{\beta, \alpha; \mu, \nu} a_{\beta, \alpha, k}^\dagger a_{\mu, \nu, q}^\dagger a_{\mu, q, -\alpha, \beta} a_{\nu, -\mu, -q},
\]

then the pairing potential can be expressed as the average

\[
    \Delta_{\alpha, \beta}(k) = \frac{1}{N} \sum_{q} \sum_{\mu, \nu} V(k, q)_{\beta, \alpha; \mu, \nu} \Phi_{\mu, \nu}(q).
\]

The above equation shows that the symmetry of the pairing potential is related to the pairing function. By analogy to Eqn. (10.47), one can then write the pairing potential as

\[
    \Delta_{\alpha, \beta}(k) = \frac{1}{2} \left[ \left( D(k) + \sigma_y \sigma^t \right) i \sigma_y \right]_{\alpha, \beta}.
\]

The three different \( S_z \) components of the spin triplet pairing potential are assigned the amplitudes which are related to the components of \( \bar{d}^t \) via

\[
    \begin{align*}
        -d_{S_z=1} &= d_x - i d_y, \\
        d_{S_z=0} &= d_z, \\
        d_{S_z=-1} &= d_x + i d_y.
    \end{align*}
\]

One can expand the singlet pairing potential in the spherical harmonics \( Y^l_m(\hat{k}) \) as

\[
    D(k) = \sum_{l, m} D^l_m(k) Y^l_m(\hat{k}),
\]

where due to the symmetry imposed by fermion anti-commutation relations \( D(k) = D(-k) \), only even values of \( l \) contribute. Likewise, the components of the triplet pairing potential can also be expanded in the same way

\[
    d_{S_z}(k) = \sum_{l, m} d^l_{m, S_z}(k) Y^l_m(\hat{k}),
\]

(10.55)
Fig. 10.20. Positions of the lines of nodes for $d$-wave superconductors, in momentum space. The dashed lines represent the lines of zeros of the superconducting order parameter on the spherical Fermi surface (indicated by the solid line). (a) The lines of nodes of the $d_{x^2-y^2}$ order parameter consists of a pair of great circles which intersect at the poles. (b) The lines of nodes for the $d_{2z^2-r^2}$ phase consists of two non-intersecting circles.

but as the pairing potential is anti-symmetric in $k$ $d_{x^2-y^2}(k) = -d_{x^2-y^2}(-k)$, only the odd values of $l$ contribute. Thus, singlet pairing only occurs with even values of $l$ and triplet pairing only occurs with odd values of $l$. It is noted that in anisotropic crystals, singlet and triplet pairing remain mutually exclusive if the symmetry group contains an inversion symmetry $k \rightarrow -k$.

The BCS mean-field Hamiltonian [125] can be expressed in terms of the pairing potentials as

$$
\hat{H}_{MF} = \sum_{\alpha, \pm} \left( e_{\alpha}(k) - \mu \right) a_{\alpha, k}^\dagger a_{\alpha, k} + \sum_{\alpha, \beta, \pm} \left( \Delta_{\alpha, \beta}(k) a_{\beta, -k}^\dagger a_{\alpha, k} + \Delta_{\alpha, \beta}^*(k) a_{\alpha, k} a_{\beta, -k} \right).$$

(10.56)
This apart from a constant term, can be re-expressed as

\[
\hat{H}_{MF} = \frac{1}{2} \left[ \sum_{\alpha, k} (e_\alpha(-k) - \mu) a_{\alpha, -k}^\dagger a_{\alpha, -k} - \sum_{\alpha, k} (e_\alpha(k) - \mu) a_{\alpha, k} a_{\alpha, k}^\dagger \right] \\
+ \sum_{\alpha, \beta, k} \left( \Delta_{\alpha, \beta}(k) a_{\beta, -k}^\dagger a_{\alpha, k}^\dagger + \Delta^*_{\alpha, \beta}(k) a_{\alpha, k} a_{\beta, -k} \right) .
\] (10.57)

A four component column operator, \(\Psi\), is introduced

\[
\Psi(k) = \begin{pmatrix}
a_{1, -k} \\
a_{1, -k}^\dagger \\
a_{1, k} \\
a_{1, k}^\dagger
\end{pmatrix},
\]

where the first two components (and the last two) are conjugate pairs, whereas the first and fourth (and second and third) are time reversal partners. This notation allows the BCS Hamiltonian to be written in matrix form

\[
\hat{H}_{MF} = \frac{1}{2} \sum_k \Psi^\dagger(k) \hat{H}_{MF}(k) \Psi(k)
\] , (10.58)

where the matrix is given by

\[
\hat{H}_{MF}(k) = 
\begin{pmatrix}
e_1(-k) & 0 & -d_{S_z=1}(k) & d_{S_z=0}(k) + D(k) \\
0 & e_1(-k) & d_{S_z=0}(k) - D(k) & d_{S_z=-1}(k) \\
-d_{S_z=1}(k) & d_{S_z=0}(k) - D^*(k) & -e_1(k) & 0 \\
d_{S_z=0}(k)^* + D^*(k) & d_{S_z=-1}(k)^* & 0 & -e_1(k)
\end{pmatrix}
\] . (10.59)

This mean-field Hamiltonian has quasi-particle excitation energies that can be expressed as

\[
E_{\sigma, k} = \pm \sqrt{(e(k) - \mu)^2 + |D(k)|^2 + |\overrightarrow{d}(k)|^2 - \sigma \left| i \overrightarrow{d}(k) \wedge \overrightarrow{d}^*(k) \right|},
\] (10.60)

where \(\sigma = \pm 1\). Consider the term inside the square root that is proportional to a vector product and \(\sigma\), this term is real. When the vector product is zero
the pairing is said to be unitary, and when it is non–zero the pairing is non–unitary. In the non–unitary state, the spin degeneracy is lifted and a staggered spin density will occur, which is a consequence of the spontaneous breaking of time reversal symmetry.

One important characteristic of unconventional superconductivity is that the gap at the Fermi surface may vanish for specific \( k \) values, which are the nodes of the order parameter. For singlet superconductivity, the gap vanishes when \( | D(\mathbf{k}) |^2 = 0 \) at the Fermi surface \( \epsilon(\mathbf{k}) = \mu \). For triplet superconductivity, the gap vanishes when

\[
| \bar{d}(\mathbf{k}) |^2 \pm | i \bar{d}(\mathbf{k}) \wedge \bar{d}^*(\mathbf{k}) | = 0
\]

at \( \epsilon(\mathbf{k}) = \mu \). In the non–unitary state, it is possible that the gap may vanish for only one spin direction.

The vanishing of the superconducting gap at the nodes does produce a finite density of states for quasi–particle excitations that may be revealed in thermodynamic, transport, and spectroscopic measurements. Although several experiments were performed with the intention of establishing the existence of and characterizing the nodes, the results were often conflicting. In retrospect, the lack of consensus concerning the nature of the nodes is not surprising as even Nb based superconductors show various deviations from strict singlet \( s \)–wave BCS behavior.

For singlet \( s \)–wave superconductivity in an isotropic system, there are no nodes. Thus, for an isotropic singlet superconductor, the existence of nodes is related to the formation of pairs with non–zero angular momenta. The singlet pairing \( d \)–wave state, \( d_{x^2−y^2} \), seems increasingly certain to be the symmetry of the high temperature superconducting phase of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \), which has an extremely anisotropic perovskite structure. The order parameter for this phase has the long wavelength form \( D(\mathbf{k}) \propto (k_x^2 - k_y^2) \), and so the gap vanishes at lines of nodes which form two great circles with a relative orientation of \( \pi/2 \) and the circles intersect at the poles as shown in Fig. 10.20a. Another type of \( d \)–wave ordering is the \( d_{2z^2−r^2} \) in which there are two separate planes where \( D(\mathbf{k}) = 0 \) that intersect with Fermi energy in circles. As shown in Fig. 10.20b, one circle is in the \( k_z = + k_f/\sqrt{3} \) plane and the other in the \( k_z = - k_f/\sqrt{3} \) plane.

There are three triplet \( p \)–wave states which have been extensively studied in the context of \( ^3\text{He} \). These are all unitary states, and the first one we shall consider is given by

\[
\overrightarrow{d}(\mathbf{k}) \propto \hat{x} k_x + \hat{y} k_y + \hat{z} k_z
\]

which corresponds to the Balian–Werthamer (BW) phase [141]. This pairing corresponds to one with angular momentum \( \overrightarrow{J} = \overrightarrow{L} + \overrightarrow{S} = 0 \), as can be

\[\footnote{The diagonal part of the self–energy has been neglected.} \]
The line of nodes of the order parameter for the polar phase of a $p$-wave superconductor is located on the equatorial circle on the Fermi surface seen from re-writing the gap function as

$$
\overrightarrow{\delta (k)} \propto k \left( \sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z} \right) 
\propto \sqrt{\frac{2}{3}} k \left[ \left( \hat{x} - i \hat{y} \right) Y_1^1 - \left( \hat{x} + i \hat{y} \right) Y_{-1}^1 + \sqrt{2} \hat{z} Y_0^1 \right]
$$

which, on comparing with Eqn. (10.49) and noting the normalization of $\Phi_{S_z=0}$, is easily identifiable as a state with $\overrightarrow{J} = 0$. The gap has a constant magnitude over the Fermi energy, and so the gap does not vanish for any $\overrightarrow{k}$ values in the BW state. The BW pairing is realized in the B phase of superfluid $^3$He.

Another state is the Anderson–Brinkman–Morell (ABM) phase [142],

$$
\overrightarrow{\delta (k)} \propto \hat{z} (k_x + i k_y) = \hat{z} k \sin \theta \exp[i \varphi]
$$

which is identified as the state with $S_z = 0$ and $L_z = \hbar$. Thus, $\overrightarrow{S}$ and $\overrightarrow{L}$ are perpendicular to each other. For the ABM phase, the gap at the Fermi surface vanishes at the point nodes where $k_x = k_y = 0$. The ABM pairing is realized in the A phase of superfluid $^3$He.

The third state is the polar phase, $p_z$, where

$$
\overrightarrow{\delta (k)} \propto \hat{z} k_z.
$$

This state has $S_z = 0$ and $L_z = 0$. As shown in Fig. 10.21, the gap function vanishes at the line node in the equatorial plane where $k_z = 0$.

The above singlet and triplet states may be appropriate for isotropic systems but are not appropriate for crystals of lower symmetry. However, due
to a symmetry breaking transition, the Cooper pairs may still have a point group symmetry lower than the full point group symmetry of the crystalline lattice. The various possible types of pairings in crystalline environments of different symmetries with spin–orbit coupling have been tabulated by Anderson [143], Volovik and Gor’kov [140], and also by Blount [139]. The possible pairings, neglecting spin–orbit coupling, were enumerated by Ozaki et al. [144]. We shall first discuss the effect of the periodic lattice and then the effect of spin–orbit coupling.

Crystal Symmetry

The periodic symmetry of the crystalline lattice breaks full rotational symmetry and, therefore, angular momentum is no longer a good quantum number. The basis functions of the rotational group can no longer be used to describe the pairing. However, the basis functions appropriate to the point group can be used. We shall focus the discussion on the \( O_h \) group, the tetragonal group \( D_{4h} \), and the hexagonal group \( D_{6h} \), which are relevant to \( \text{UBe}_13 \), \( \text{CeCu}_2\text{Si}_2 \) and \( \text{URu}_2\text{Si}_2 \), and \( \text{UPt}_3 \). For an irreducible representation with dimensionality \( d \), the scalar or vector order parameter can be expressed as a linear combination of the degenerate partner basis functions \( \phi_i(\hat{k}) \) (scalar or vector), times functions of the invariants of the full point group \( f_n(\hat{k}) \). The degenerate partners are expressed in the form \( \sum_n \phi_{i,n}(\hat{k}) f_n(\hat{k}) \). Thus, for example, the vector order parameter is expressed as

\[
\vec{d}(\hat{k}) = \sum_{i=1}^{i=d} C_i \left[ \sum_n \vec{\phi}_{i,n}(\hat{k}) f_n(\hat{k}) \right] \quad (10.66)
\]

and an analogous equation holds true for the singlet order parameter \( D(\hat{k}) \). The summation over \( n \) runs through \( d \) and \( 3d \) values respectively, for singlet and triple pairings [145]. A specific example found in Table(10.2) for singlet pairing in cubic symmetry is the doubly degenerate \( \Gamma_3^+ (E_g) \) representation in which the degenerate partners basis functions have the form

\[
\phi_1(\hat{k}) = \sum_{n=2;4} (k_x^n + k_y^n - 2k_z^n) f_n(\hat{k}) ,
\]

\[
\phi_2(\hat{k}) = \sum_{n=2;4} (k_x^n - k_y^n) , f_n(\hat{k}) \quad (10.67)
\]

where the \( f_n(\hat{k}) \) have the form \( a_n + b_n k^2 + c_n (k_x^4 + k_y^4 + k_z^4) + \ldots \). Likewise, for cubic symmetry, the singly-degenerate triplet pairing \( \Gamma_1^- (A_1u) \) representation found in Table(10.3) has the basis function

\[
\vec{\phi}_1(\hat{k}) = \sum_{n=1;3;5} (\hat{x} k_x^n + \hat{y} k_y^n + \hat{z} k_z^n) f_n(\hat{k}) . \quad (10.68)
\]

\(^5\) It is possible that the functions \( f_n(\hat{k}) \) vanish at some \( \hat{k} \) points, thereby producing nodes in the order parameter. However, the set of nodes that are produced in this way will still have the full point group symmetry of the lattice.
The coefficients $C_i$ multiplying the degenerate partner basis functions are arbitrary and are determined only by the spontaneous symmetry broken state. The invariant functions $f_n(\hat{k})$ corresponding to the admixtures of the different angular momentum components are well defined for each representation and should be determined by minimization of the free energy. The tetragonal symmetry singlet and triplet representation basis functions are given in Table(10.4) and Table(10.5) respectively. The basis for the non–degenerate singlet pairings in the tetragonal $\Gamma_3^+ (B_{1g})$ representation is written, with different notation $k_\pm = k_x \pm ik_y$, as

$$\phi_1(\hat{k}) = (k_x^2 - k_y^2) f(\hat{k}) = Re k_+^2 f(\hat{k}) ,$$

(10.69)

where the expansion of the invariant function no longer has a quadratic term in the modulus of $\hat{k}$ but instead, has the different form $f(\hat{k}) = a + bk_x^2 + c(k_x^2 + k_y^2) + \ldots$. The triplet pairing in a $D_{4h}$ structure belonging to the representation $\Gamma_1^- (A_{1u})$ has the form given by,

$$\overline{\phi}_1(\hat{k}) = \hat{z}k_z f_0(\hat{k}) + \sum_{n=1;3} (\hat{x}k_x^n + \hat{y}k_y^n) f_n(\hat{k}) .$$

(10.70)

Even though the crystal field mixes states of different angular momentum, one can usually identify the pairing states via the dominant components of the orbital angular momentum. For example, in the cubic group with spin singlet pairing shown in Table(10.2), we identify the nodeless one dimensional $\Gamma_1^+ (A_{1g})$ representation with $s$–wave pairing and the lowest components of the $\Gamma_3^+ (E_g) (n = 2)$ and $\Gamma_5^+ (T_{2g}) (n = 0)$ representations as the crystal field split members of the five dimensional $d$–wave pairing basis. Likewise, for triplet pairing in the cubic group shown in Table(10.3), we can identify the one dimensional basis (formed by selecting the $n = 1$ component) of $\Gamma_1^- (A_{1u})$ and the two dimensional basis (also formed by selecting $n = 1$) of $\Gamma_3^- (E_u)$ as the crystal field split three dimensional $p$–wave pairing basis functions.

The node structure for the non–degenerate representations can be found. For example, in a cubic structure with singlet pairing, the high symmetry reduces the number of non–degenerate representations to two. These are the $\Gamma_1^+ (A_{1g})$ phase, which is nodeless and the $\Gamma_2^+ (A_{2g})$ phase, where the order parameter vanishes on six distinct planes. In the $\Gamma_2^+ (A_{2g})$ phase, the six planes intersect the three dimensional Fermi surface on six distinct arcs, giving six lines of nodes on the Fermi surface. In a structure with lower symmetry such as the tetragonal structure, the number of non–degenerate singlet representations is four. The possible singlet phases in $D_{4h}$ are shown in Table(10.4). In addition to the nodeless $\Gamma_1^+ (A_{1g})$ phase, one finds the two non degenerate $\Gamma_3^+ (B_{1g})$, and $\Gamma_4^+ (B_{2g})$ phases, which each produce two lines of nodes as expected for $d$–wave pairing, and finally the order parameter for the $\Gamma_2^+ (A_{2g})$ pairing vanishes on four planes giving four lines of nodes.

For triplet pairing, the occurrence of nodes is generally rarer than for singlet pairings since the three components of $\hat{d}(k)$ must vanish simultane-
Table 10.2. Singlet Pairing Basis Functions for in the Cubic Group $O_h$. The forms of the degenerate partners are shown. As explained in the text, the components labelled by $n$ must be multiplied by an invariant function $I_n(k)$ and summed over $n$ to yield a degenerate partner. The degenerate partners are separated by commas.

<table>
<thead>
<tr>
<th>Representation</th>
<th>Basis Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^+<em>1(A</em>{1g})$</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^+<em>2(A</em>{2g})$</td>
<td>$(k_x^2 - k_y^2)(k_y^2 - k_z^2)(k_z^2 - k_x^2)$</td>
</tr>
<tr>
<td>$\Gamma^+_3(E_g)$</td>
<td>$2k_x^n - k_y^n - k_z^n$, $k_y^n - k_z^n$, $k_z^n - k_x^n$ $n = 2; 4$</td>
</tr>
<tr>
<td>$\Gamma^+<em>4(T</em>{1g})$</td>
<td>$k_xk_y(k_x^n - k_y^n)$, $k_yk_z(k_y^n - k_z^n)$, $k_zk_x(k_z^n - k_x^n)$ $n = 2; 4; 6$</td>
</tr>
<tr>
<td>$\Gamma^+<em>5(T</em>{2g})$</td>
<td>$k_xk_yk_z^n$, $k_yk_zk_x^n$, $k_zk_xk_y^n$ $n = 0; 2; 4$</td>
</tr>
</tbody>
</table>

...ously. The need to satisfy three conditions may be expected to reduce the dimensions of the nodes from a surface to a set of isolated points, which need not lie on the Fermi surface. Inspection of Table(10.3) shows that this is the case for the $O_h \Gamma^-_1(A_{1u})$ phase where the components vanish on orthogonal planes producing isolated zeros not on the Fermi surface, so the gap has no nodes. The components of the order parameter for the highly symmetric non–degenerate $\Gamma^-_2(A_{2u})$ phase each vanish on three planes. This leads to the order parameter vanishing on the four lines $k_x = \pm k_y = \pm k_z$, which intersect the Fermi surface in eight points, resulting in eight point nodes.

The detailed node structure of degenerate representations depends on the spontaneous symmetry breaking between the degenerate partners. In the singlet case, the phase of the order parameter $D(k)$ can always be chosen to be zero and so $D(k)$, if it vanishes, does so on surfaces that intersect the Fermi surface in curves. Examples of this are found in both the triply degenerate $O_h \Gamma^-_1(A_{1u})$ and the doubly degenerate $\Gamma^+_3(E_g)$ singlet pairing representations. It is seen that if the system spontaneously selects any one of the degenerate partners, the order parameter will vanish on two distinct planes leading to two lines of nodes. Also, if the effects of the higher order angular momentum contributions are minimal, an arbitrary linear combination of degenerate partner basis functions also makes the order parameter vanish on two surfaces leading to two curved lines of nodes. The analogous case for the singlet $D_{4h}$ symmetry is given by the doubly degenerate $\Gamma^+_3(E_g)$ representation, which also can yield lines of nodes. One of the line nodes is the intersection of the plane $k_z = 0$ with the Fermi surface.
Basis Functions, (2 Fermi surface. An example of this is given in the irreducible representation where, if \( \mathbf{k} \) of independent components of achieved since the rotational invariance in spin space can reduce the number has noted [139], the vanishing of the order parameter on a surface can be isolated nodes at the poles. direction, then \( \mathbf{k} \) symmetry, as in the tetragonal requirement that if \( \mathbf{d} \) to two and thus lead to a line of nodes on the Fermi surface. An example of this is given in the \( O_h \) group with the irreducible representation where, if \( \mathbf{d} \) spontaneously chooses to lie in the \( \mathbf{k} \) direction, then \( \mathbf{d}(\mathbf{k}) \) vanishes on two surfaces and leads to two lines of nodes.

### Table 10.3. Triplet Pairing Basis Functions in the Cubic \( O_h \) group.

<table>
<thead>
<tr>
<th>Representation</th>
<th>Basis Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{v}^{-}(A_{1u}) )</td>
<td>( \hat{x}k_x^n + \hat{y}k_y^n + \hat{z}k_z^n )</td>
</tr>
<tr>
<td>( \Gamma_{v}^{-}(A_{2u}) )</td>
<td>( \hat{x}k_x^n(k_2^n - k_4^n) + \hat{y}k_y^n(k_2^n - k_4^n) + \hat{z}k_z^n(k_2^n - k_4^n) )</td>
</tr>
<tr>
<td>( \Gamma_{v}^{-}(E_u) )</td>
<td>( \hat{x}k_x^n - \hat{y}k_y^n, \hat{x}k_x^n + \hat{y}k_y^n - 2\hat{z}k_z^n )</td>
</tr>
<tr>
<td>( \Gamma_{v}^{-}(T_{1u}) )</td>
<td>( k_x^n(\hat{y}k_y^n - \hat{z}k_z^n), k_y^n(\hat{z}k_z^n - \hat{x}k_x^n), k_z^n(\hat{x}k_x^n - \hat{y}k_y^n) )</td>
</tr>
<tr>
<td>( \Gamma_{v}^{-}(T_{2u}) )</td>
<td>( k_x^n(\hat{y}k_y^n + \hat{x}k_x^n), k_y^n(\hat{z}k_z^n + \hat{x}k_x^n), k_z^n(\hat{y}k_y^n + \hat{z}k_z^n) )</td>
</tr>
</tbody>
</table>

With triplet pairing, the phase of the order parameter can also be chosen to be real in the unitary case. However, in this case, due to the stringent requirement that if \( \mathbf{d}(\mathbf{k}) \) is to vanish, three equations to be satisfied, the only nodes which occur usually are point nodes. These may be satisfied by symmetry, as in the tetragonal \( \Gamma_{v}^{-}(A_{2u}) \) pairing shown in Table(10.5) where, if \( f_2 = f_3 = 0 \), symmetry dictates that the order parameter vanishes on the line \( k_x = k_y = 0 \). In this case, the gap that develops on the Fermi surface has isolated nodes at the poles.

However, line nodes also can be obtained for triplet phases. As Blount has noted [139], the vanishing of the order parameter on a surface can be achieved since the rotational invariance in spin space can reduce the number of independent components of \( \mathbf{d} \) to two and thus lead to a line of nodes on the Fermi surface. An example of this is given in the \( O_h \) group with the irreducible representation where, if \( \mathbf{d} \) spontaneously chooses to lie in the \( \mathbf{k} \) direction, then \( \mathbf{d}(\mathbf{k}) \) vanishes on two surfaces and leads to two lines of nodes.
Table 10.4. Singlet Pairing Basis Functions in the Tetragonal $D_{4h}$ group.

<table>
<thead>
<tr>
<th>Representation</th>
<th>Basis Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1^+ (A_{1g})$</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2^+ (A_{2g})$</td>
<td>$k_y k_z (k_x^2 - k_y^2)$</td>
</tr>
<tr>
<td>$\Gamma_3^+ (B_{1g})$</td>
<td>$k_z^2 - k_y^2$</td>
</tr>
<tr>
<td>$\Gamma_4^+ (B_{2g})$</td>
<td>$k_z k_y$</td>
</tr>
<tr>
<td>$\Gamma_5^+ (E_g)$</td>
<td>$k_z k_x ; k_z k_y ; k_z k_x^3 ; k_z k_y^3$</td>
</tr>
</tbody>
</table>

on the Fermi surface. This type of situation is expected to be forbidden when the effect of spin–orbit coupling is taken into consideration. The irreducible

Table 10.5. Triplet Pairing Basis Functions in the Tetragonal $D_{4h}$ group. The value $k_x \pm i k_y$ is denoted by $k_\pm$ and the vector $\hat{x} \pm i \hat{y}$ is denoted by $\hat{r}_\pm$. The upper and lower signs $\pm$ in the doubly degenerate $E_u$ representation correspond to the degenerate partners $(n = 0 ; 2)$.

<table>
<thead>
<tr>
<th>Representation</th>
<th>Basis Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1^+ (A_{1u})$</td>
<td>$\hat{z} k_z ; \text{Re} \hat{r}<em>- k</em>+ ; \text{Re} \hat{r}<em>+ k</em>+^3$</td>
</tr>
<tr>
<td>$\Gamma_2^+ (A_{2u})$</td>
<td>$\text{Im} \hat{r}<em>- k</em>+ ; \text{Im} \hat{r}<em>+ k</em>+^3 ; \hat{z} k_z \text{Im} k_+^4$</td>
</tr>
<tr>
<td>$\Gamma_3^+ (B_{1u})$</td>
<td>$\hat{z} k_z \text{Re} k_+^2 ; \text{Re} \hat{r}<em>+ k</em>+ ; \text{Re} \hat{r}<em>- k</em>+^3$</td>
</tr>
<tr>
<td>$\Gamma_4^+ (B_{2u})$</td>
<td>$\hat{z} k_z \text{Im} k_+^3 ; \text{Im} \hat{r}<em>+ k</em>+ ; \text{Im} \hat{r}<em>- k</em>+^3$</td>
</tr>
<tr>
<td>$\Gamma_5^+ (E_u)$</td>
<td>$\hat{z} k_\pm^{n+1} ; k_z \hat{r}<em>\pm k</em>\pm^n ; k_z \hat{r}<em>\pm k</em>\pm^{n+2}$</td>
</tr>
</tbody>
</table>

representations for singlet and triplet pairings of the hexagonal group $D_{6h}$ are shown in Table(10.6) and Table(10.7).

In addition to the point group symmetry, the superconducting order parameter must also have the same translational symmetry as the lattice. In particular, the order parameter must be periodic in the Brillouin zone and should also reflect any other translation symmetry element present in the space group. The functions given in the tables correspond to the long wavelength limit form of the order parameters. Some possible forms of the order
parameters with the correct translational symmetry have been examined for the case of UPt$_3$ [146, 147].

Table 10.6. Singlet Pairing Basis Functions in the Hexagonal $D_{6h}$ group. The value $k_x \pm i k_y$ is denoted by $k_\pm$. The upper and lower signs $\pm$ in the doubly degenerate $E_g$ representations correspond to the degenerate partners.

<table>
<thead>
<tr>
<th>Representation</th>
<th>Basis Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1^+(A_{1g})$</td>
<td>$1$</td>
</tr>
<tr>
<td>$\Gamma_2^+(A_{2g})$</td>
<td>$Im\ k_+^6$</td>
</tr>
<tr>
<td>$\Gamma_3^+(B_{1g})$</td>
<td>$k_z\ Im\ k_+^3$</td>
</tr>
<tr>
<td>$\Gamma_4^+(B_{2g})$</td>
<td>$k_z\ Re\ k_+^3$</td>
</tr>
<tr>
<td>$\Gamma_5^+(E_{1g})$</td>
<td>$k_z\ k_\pm$ ; $k_z\ k_+^5$</td>
</tr>
<tr>
<td>$\Gamma_6^+(E_{2g})$</td>
<td>$k_\pm^2$ ; $k_\pm^4$</td>
</tr>
</tbody>
</table>

Spin–Orbit Coupling

In the presence of spin–orbit coupling, the electrons spin quantized about any fixed axis is no longer a good quantum number, however, the electron does have a well defined magnetic moment. The magnetic moment is an axial vector and can be expressed in terms of a $k$ dependent gyromagnetic ratio $g_{i,j}$ which couples to the electron spins via

$$m_i(k) = \frac{1}{2} \sum_j g_{i,j}(k) \sigma_j . \quad (10.71)$$

Then, in second quantized form, the magnetic moment operator is given by the expression

$$\hat{M}(k) = \frac{1}{2} \sum_{\alpha,\beta} a_\alpha^\dagger(k) \left( \bar{m}(k) \right)_{\alpha,\beta} a_\beta(k) \quad (10.72)$$

The expectation value of this operator can be expressed in terms of the one–electron density matrix $\rho_{\alpha,\beta}(k) = <a_\alpha^\dagger(k)\ a_\beta(k)>$, as

$$<| \hat{M}(k) | > = Trace \left[ \bar{m}(k) \rho(k) \right] . \quad (10.73)$$

Since the Zeeman splitting of the electron in a Bloch state $k$ is given by the eigenvalues, $\pm E_z(k)$, of the Hamiltonian

$$H_Z = -\hat{M}(k) \cdot \vec{H} . \quad (10.74)$$
The results derived in the presence of spin–orbit coupling go smoothly over into the zero spin–orbit case, as can be seen by expressing the order parameter

\[ \Delta_{\alpha,\beta}(k) = \left( \begin{array}{c} D(k) + \bar{d}(k) \cdot \bar{m}(k) \end{array} \right) (i \sigma_y) \right)_{\alpha,\beta}. \]

The results derived in the presence of spin–orbit coupling go smoothly over into the zero spin–orbit case, as can be seen by expressing the order parameter in the form

\[ \Delta^1(k) \Delta(k) = \left| D(k) \right|^2 + \left( \bar{m}(k) \cdot \bar{d}(k) \right) \left( \bar{d}^*(k) \cdot \bar{m}(k) \right). \]
With the use of the Pauli identity, this procedure yields the same expression for the quasi-particle eigenvalues as Eqn. (10.60), but in which $\tilde{d}(\vec{k})$ is merely replaced by $\tilde{d}(\vec{k}) g(\vec{k})$. Thus, most of the formal results for the superconducting quasi-particles found without spin-orbit coupling also hold when it is present. In particular, one expects that the characteristic energy dependence of the superconducting quasi-particle density of states will be unaffected by spin-orbit scattering.

**Quasi-Particle Density of States**

The density of states for single quasi-particle excitations for anisotropic superconducting states have distinctly different forms which are determined by whether the gap is nodeless, has isolated nodes, or lines of nodes and also the slope with which the gap falls to zero. The quasi-particle density of states $\rho_{qp}(E)$ is given by

$$\rho_{qp}(E) = \frac{1}{2} \sum_{\vec{k}, \pm} \delta(E \pm E_{\sigma, \vec{k}}).$$

(10.78)

On assuming singlet $s$-wave pairing, one finds the BCS result

$$\rho_{BCS}(E) = \rho(\mu) \frac{|E|}{\sqrt{E^2 - |\Delta_0|^2}}$$

(10.79)

for $|E| > \Delta_0$, otherwise $\rho_{BCS}(E) = 0$. Here $\rho(\mu)$ is the normal phase density of states that has been assumed to be constant near the Fermi energy and $D(k_F) = \Delta_0$. Since this $s$-wave phase shows a gap of width $2 |\Delta_0|$ all the way around the position of the normal state Fermi surface, a number of physical quantities show simple exponentially activated behavior in the low temperature regime where the temperature dependence of the superconducting gap is small. For the anisotropic singlet $d_{x^2-y^2}$ pairing, the density of states is given by

$$\rho_{d_{x^2-y^2}}(E) = \rho(\mu) \frac{|E|}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{\sin \theta}{\sqrt{E^2 - |\Delta_0|^2 \sin^4 \theta \cos^2 2\phi}}.$$  

(10.80)

As the order parameter vanishes on two great circles, $\cos 2\phi = 0$, on the Fermi surface, the density of states is proportional to $E \ln E$ as $E/\Delta_0 \rightarrow 0$. The $d_{x^2-y^2}$ order parameter of a cubic material also has two lines of nodes, which results in the density of states

$$\rho_{d_{x^2-y^2}}(E) = \rho(\mu) \frac{|E|}{2} \int_0^\pi d\theta \frac{\sin \theta}{\sqrt{E^2 - \frac{1}{4} |\Delta_0|^2 (1 - 3 \cos^2 \theta)^2}}.$$  

(10.81)

that also tends to zero linearly for small $E$. The quasi-particle density of states for these particular singlet phases are shown in Fig. 10.22. The quasi-particle density of states for the phases $d_{x,y}$, $d_{x,z}$ and $d_{y,z}$ should be identical.
Fig. 10.22. The quasi–particle density of states $\rho_{qp}(E)$ for selected singlet superconducting phases, in the clean limit. The BCS $s$–wave state has a true gap in the quasi–particle density of states, and a singularity at the gap edge. The maximum superconducting gap is denoted by $\Delta_0$. The $d$–wave phases have states with energies below $\Delta_0$.

with $\rho_{d_{x^2-y^2}}(E)$. For an isotropic system, the most stable $d$–wave phase [128] corresponds to a linear combination of the even $m$ order parameters

$$D(\hat{k}) \propto \left[ \frac{1}{\sqrt{2}} Y_2^0(\hat{k}) + \frac{1}{2} \left( Y_2^2(\hat{k}) - Y_{-2}^2(\hat{k}) \right) \right]$$

which only has point nodes. Therefore, the quasi–particle density of states varies as $E^2$ for small $E$, as shown in Fig. 10.23.

For triplet pairing, the differing node structures yield different forms for the quasi–particle density of states. The density of states is given in terms of an integration over the direction of $\hat{k}$,

$$\rho_{S=1}(E) = \frac{1}{8\pi} \rho(\mu) \int d\Omega \sum_{\sigma} \text{Re} \left[ \frac{|E|}{\sqrt{E^2 + |\hat{d}(\hat{k})|^2 - \sigma i \hat{d}(\hat{k}) \wedge \hat{d}^*(\hat{k})|}} \right].$$

We shall describe the relation between the order parameter and the quasi–particle density of states for the well known $p$–wave states. The BW state, having an isotropic gap and no nodes, has the same density of states as the singlet $s$–wave phase given by the BCS expression, but where $\Delta_0$ is given by the magnitude of $\hat{d}$ at the position of the normal state Fermi surface.
The ABM state order parameter given in spherical polar coordinates is \( \vec{d} = \hat{z} \Delta_0 \sin \theta e^{i \phi} \), and so the quasi–particle density of states in the ABM phase is found from

\[
\rho_{ABM}(E) = \frac{\rho(\mu) |E|}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{\sin \theta}{\sqrt{E^2 - |\Delta_0|^2 \sin^2 \theta}} \\
= \frac{\rho(\mu) E}{2\Delta_0} \ln \left| \frac{E + \Delta_0}{E - \Delta_0} \right|. \tag{10.84}
\]

Thus, the density of states in the ABM phase has a weak logarithmic singularity at \( E = \Delta_0 \) and falls to zero as \( E \to 0 \) like \( E^2 \), due to the presence of isolated nodes. In the polar state, \( \vec{d} = \hat{z} \Delta_0 \cos \theta \), so the density of states is given by

\[
\rho_p(E) = \frac{\rho(\mu) |E|}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{\sin \theta}{\sqrt{E^2 - |\Delta_0|^2 \cos^2 \theta}} \\
= \frac{\pi \rho(\mu) |E|}{2\Delta_0} \Delta_0 > |E| \\
= \frac{\rho(\mu) E}{\Delta_0} \arcsin \left[ \frac{\Delta_0}{E} \right] \quad \Delta_0 < |E|. \tag{10.85}
\]

Thus, due to the presence of a line of nodes in the polar phase, the quasi–particle density of states at lower energies only falls to zero linearly in \( E \), as \( E \to 0 \). This should be contrasted with the ABM phase, which has isolated point nodes where the density of states goes to zero quadratically with \( E \). The larger density of states at low energies for polar phase with its line nodes compared with the ABM phase with its point nodes, is compensated by the decrease in the peak of the quasi–particle density of states. That is, the polar state only shows a slight enhancement at \( \Delta_0 \) where the density of states only has a cusp, but the ABM state shows a divergence. The quasi–particle density of states for the singlet BCS state is shown together with the \( d_{x^2-y^2} \) state and the \( d_{x^2-y^2} \) in Fig. 10.22. The singularities and cusps are due to the gaps having extremal points at the position of the normal state Fermi surface. The quasi–particle density of states for the triplet BW, ABM, and polar states are shown in Fig. 10.24. The low–energy behavior of these quasi–particle density of states are quite distinct, having different power law dependences in \( E \). The different power laws are due to the differences in the node structure of the superconducting gap. These power law dependences may be expected to show up in thermodynamic properties far below \( T_c \), albeit modified by the effects of impurity scattering and collective excitations.

**Pair Breaking Impurities**

In an \( s \)-wave superconductor, the effect of non–magnetic impurities is min-
Fig. 10.23. The quasi–particle density of states $\rho_d(E)$ for an isotropic $d$–wave phase, with the order parameter $|D(\hat{k})| = \Delta_0 \left[ \sqrt{2} Y_0^2 \right.$ \ $+ \left. ( Y_2^2 - Y_4^2 ) \right]$. Since the order parameter has eight point nodes as the quasi–particle density of states is proportional to $E^2$ for small $E$. Also, since the order parameter only attains its maximum value of $\Delta_0$ at six isolated points, the density of states does not diverge.

The variation of $T_c$ for Sn with a concentration of In impurities was studied by Coles [149]. The $T_c$ showed a sharp initial drop which saturated for In concentrations of about 2%. The initial drop of $T_c$ is attributed to the impurities destroying the anisotropy of the Fermi surface. This is not a violation of Anderson’s theorem since it strictly only applies to systems with isotropic Fermi surfaces. The almost constant value of $T_c$ which is found for In concentrations greater than 2% is a verification of Anderson’s theorem.
Fig. 10.24. The quasi–particle density of states $\rho_{qp}(E)$ for selected triplet $p$–wave superconducting states, in the clean limit. The density of states of the BW phase is identical to that of the BCS $s$–wave phase. The ABM phase and polar phases have states below $\Delta_0$. The ABM or axial state shows a quadratic energy dependence for energies below $\Delta_0$, while the polar state has a linear energy dependence.

Anderson’s theorem [150], which describes the effect of non–magnetic impurities in $s$–wave superconductors, can be stated as, “A static external perturbation, that neither breaks time reversal invariance nor produces a spatial variation of the order parameter, does not produce a change in the thermodynamic properties of a superconductor.” Since the order parameters of anisotropic superconductors are inhomogeneous, Anderson’s theorem no longer applies and the effect of impurities is analogous to that of magnetic impurities in $s$–wave superconductors [151, 152]. The analogy is complete in that significant concentrations of impurities may produce significant changes in the low–energy density of states leading to the removal of any remaining gaps. The changes in the low–energy variation of the quasi–particle density of states lead to variances in the power law temperature dependences expected from analysis of the simple node structures of clean materials [153–155].

The types of effect caused by non–magnetic impurities in anisotropic superconductors can be seen by examining the density of states in the superconducting state in which the impurity potential, $U_0$, is short–ranged and is treated as a small perturbation. The density of states can be obtained from the trace of the Green’s function in the superconducting state. To treat the pairing in the superconducting state, one introduces the four by four matrix...
Green's function $G(k; \tau)$ describing the four component fields, via

$$G(k; \tau) = -\frac{1}{\hbar} < | \hat{T} \psi(k, \tau) \psi^\dagger(k, 0) | > ,$$  \hspace{1cm} (10.86)

where $\hat{T}$ is Wick's time ordering operator. The upper and lower two by two diagonal blocks have matrix elements that are related to the usual Green's functions

$$G_{\alpha,\beta}(k, k'; \tau) = -\frac{1}{\hbar} < | \hat{T} a_{k,\alpha}(\tau) a_{k',\beta}^\dagger(0) | > .$$  \hspace{1cm} (10.87)

The upper and lower two by two off-diagonal blocks represent the anomalous Green's functions, as introduced by Gor'kov [148]. The elements of the anomalous Green's functions are written as

$$F_{\alpha,\beta}(k, k'; \tau) = \frac{1}{\hbar} < | \hat{T} a_{k,\alpha}(\tau) a_{-k',\beta}(0) | >$$  \hspace{1cm} (10.88)

and

$$F_{\alpha,\beta}^\dagger(k, k'; \tau) = \frac{1}{\hbar} < | \hat{T} a_{-k,\alpha}^\dagger(\tau) a_{k',\beta}^\dagger(0) | > .$$  \hspace{1cm} (10.89)

Within the mean-field approximation, the Fourier Transform of the Green's functions are given by the solutions of the coupled equations

$$\left( i \hbar \omega_n - e(k) + \mu \right) G_{\alpha,\beta}(k, k'; i\hbar\omega_n) + \sum_{\gamma} \Delta_{\alpha,\gamma}(k) F_{\gamma,\beta}^\dagger(k, k'; i\hbar\omega_n) = \delta_{\alpha,\beta} \delta(k - k')$$  \hspace{1cm} (10.90)

and

$$\left( i \hbar \omega_n + e(k) - \mu \right) F_{\alpha,\beta}^\dagger(k, k'; i\hbar\omega_n) + \sum_{\gamma} \Delta_{\alpha,\gamma}^\ast(k) G_{\gamma,\beta}(k, k'; i\hbar\omega_n) = 0$$  \hspace{1cm} (10.91)

In the unitary states, these equations have the solution,

$$G_{\alpha,\beta}(k, k'; i\hbar\omega_n) = -\frac{(i \hbar \omega_n + e(k) - \mu)}{\hbar^2 \omega_n^2 + (e(k) - \mu)^2 + \Delta^\dagger(k) \Delta(k)} \delta_{\alpha,\beta} \delta(k - k')$$  \hspace{1cm} (10.92)

and

$$F_{\alpha,\beta}^\dagger(k, k'; i\hbar\omega_n) = +\frac{\Delta_{\alpha,\beta}^\ast(k)}{\hbar^2 \omega_n^2 + (e(k) - \mu)^2 + \Delta^\dagger(k) \Delta(k)} \delta(k - k') .$$  \hspace{1cm} (10.93)
The order parameter is determined from the non-linear equation

\[ \Delta_{\alpha,\beta}(k) = -k_B T \sum_{n,q} \sum_{\mu,\nu} V(k,q)_{\beta,\alpha,\mu,\nu} F_{\nu,\mu}(q,q; i\hbar\omega_n) \]  

(10.94)

which yields \( \Delta \) as a function of temperature. We assume a low concentration of impurities, \( c_0 \), that are randomly distributed and act as point scatterers. The matrix self-energy can be calculated as

\[ \Sigma(k; i\hbar\omega_n) = c_0 \sum_p U_0 \rho_4 G(p; i\hbar\omega_n) \rho_4 U_0, \]  

(10.95)

where \( \rho_4 \) is the 4 \( \times \) 4 Dirac matrix that is written in block diagonal form as

\[ \rho_4 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}. \]  

(10.96)

Here, \( I \) is the unit two by two matrix. The Green’s functions have to be calculated self-consistently. In the unitary case, the diagonal and non-diagonal elements in the self-energy can be evaluated and do give rise to a renormalization of the frequency and order parameter. The renormalizations are given by the solution of the coupled equations

\[ i \hbar \tilde{\omega}_n = i \hbar \omega_n + c_0 \sum_p U_0^2 \frac{i \hbar \tilde{\omega}_n + (e(p) - \mu)}{\hbar^2 \tilde{\omega}_n^2 + (e(p) - \mu)^2 + \Delta^+(p) \Delta(p)}, \]

\[ \tilde{D}_{\alpha,\beta}(k) = D_{\alpha,\beta}(k) + c_0 \sum_p U_0^2 \frac{\tilde{D}_{\alpha,\beta}(p)}{\hbar^2 \tilde{\omega}_n^2 + (e(p) - \mu)^2 + \Delta^+(p) \Delta(p)}. \]  

(10.97)

The energy \( e(p) \) is odd about the Fermi energy and so, for systems with electron–hole symmetry, the term proportional to \( e(p) - \mu \) drops out in the diagonal parts of the self-energy matrix. Thus, impurity scattering only results in a frequency dependent renormalization of \( \omega_n \). For \( s \)-wave scattering, subject to Anderson’s theorem, the off-diagonal term produces an identical frequency dependent renormalization of the gap. Thus, for \( s \)-wave scattering in the Born approximation, one finds the explicit form for the renormalizations

\[ i\tilde{\omega}_n = i\omega_n + \pi c_0 U_0^2 \rho(\mu) \frac{i\tilde{\omega}_n}{\sqrt{\hbar^2 \tilde{\omega}_n^2 + |\tilde{D}_s(k_F)|^2}}, \]

\[ \tilde{D}_s(k) = D_s(k) + \pi c_0 U_0^2 \rho(\mu) \frac{\tilde{D}_s(k_F)}{\sqrt{\hbar^2 \tilde{\omega}_n^2 + |\tilde{D}_s(k_F)|^2}}. \]  

(10.98)
Hence the ratio of $\tilde{\omega}_n/\tilde{D}_s$ is unchanged from the un-renormalized value $\omega_n/D_s$. Furthermore, the quasi-particle density of states is unaltered since it only depends upon the ratio $\tilde{\omega}_n/\tilde{D}_s$. The equation that determines the order parameter remains unchanged. Thus, the critical temperature of an $s$-wave superconductor is not substantially reduced by the presence of the impurities. These conclusions are in accord with Anderson’s theorem.

For triplet pairing, the gap is an odd function of $p$ and so, due to the summation over the direction of $p$, the off-diagonal self-energy vanishes identically. Hence, we have

$$i \tilde{\omega}_n = i \omega_n + \pi c_0 U_0^2 \rho(\mu) \int \frac{d\Omega_p}{4\pi} \frac{i \tilde{\omega}_n}{\sqrt{\hbar^2 \omega_n^2 + |\vec{d}(p)|^2}}$$

and

$$\tilde{d}(k) = \tilde{d}(k). \quad (10.99)$$

Therefore, Anderson’s theorem does not apply to triplet superconductors.

The effect of impurities reduce the critical temperature $T_c$, as can be seen from the linearized gap equation

$$1 = k_B T_c \pi \sum_{n=0}^{n_c} \frac{1}{|\hbar \omega_n|} \left( < V(k_F, k_F) > \rho(\mu) \right), \quad (10.100)$$

where the summation is cut-off at $n_c$, which is determined by a frequency range $\omega_c$ in which the pairing interaction is attractive $\hbar \omega_c = (2n_c + 1) \pi k_B T$, and $< V(k_F, k_F) >$ is the Fermi surface averaged value of the pairing interaction. The summation depends logarithmically on the cut off.

The linearized gap equation can be re-written as

$$\frac{1}{k_B T_c \pi} < V(k_F, k_F) > \rho(\mu) = \sum_{n=0}^{n_c} \frac{1}{|\hbar \omega_n|} + \sum_{n=0}^{\infty} \left( \frac{1}{|\hbar \omega_n|} + \pi c_0 |U_0|^2 \rho(\mu) \right). \quad (10.101)$$

The critical temperature obtained for the dirty system should be compared with the expression for the critical temperature $T_{c0}$ obtained for the clean system

$$1 = k_B T_{c0} \pi \sum_{n=0}^{n_c} \frac{1}{|\hbar \omega_n|} < V(k_F, k_F) > \rho(\mu). \quad (10.102)$$

On identifying the $\frac{2\pi}{\hbar} c_0 |U_0|^2 \rho(\mu)$ as being equal to the impurity scattering rate $\frac{1}{\tau}$ as evaluated in the Born approximation, and using the expression for
$T_{c0}$ for the clean system, one finds that non–magnetic impurities depress $T_c$ in an anisotropic superconductor according to

$$\ln \left( \frac{T_{c0}}{T_c} \right) = \psi \left( \frac{1}{2} + \frac{\hbar}{4 \pi k_B T_c \tau} \right) - \psi \left( \frac{1}{2} \right),$$  \hspace{1cm} (10.103)$$

where $\psi$ is the digamma function. This formula is similar to the formula derived by Abrikosov and Gor’kov that describes the depression of $T_c$ caused by spin–flip scattering by impurities in an $s$–wave superconductor [151]. The analogy to scattering by paramagnetic impurities in an $s$–wave superconductor is complete in that large enough impurity scattering can also lead to gapless superconductivity.

We shall explicitly examine the transition to the gapless phase for some triplet phases [154]. On analytically continuing from $i \hbar \omega_n \to E + i \delta$ one finds

$$\lim_{i \hbar \omega_n \to E} \Im \left[ i \hbar \tilde{\omega}_n \right] = \pi c_0 \left| U_0 \right|^2 \rho_{qp}(E),$$  \hspace{1cm} (10.104)$$

where the self–consistency equation for $s = i \hbar \tilde{\omega}_n$ is given by

$$s - E = i \frac{\hbar}{2 \tau} \int \frac{d\Omega_k}{4 \pi} \frac{s}{\sqrt{s^2 - \left| \tilde{d}(k) \right|^2}}.$$

For the Balian–Werthamer phase, where $\tilde{d}(k) = \Delta_0 \hat{k}$, the above equation reduces to

$$s - E = i \frac{\hbar}{2 \tau} \frac{s}{\sqrt{s^2 - \left| \Delta_0 \right|^2}}.$$

The gap energy is the threshold value of $E_g$ below which $s$ is real and is given by the critical value of $s$ determined from the equation

$$\frac{\partial E}{\partial s} = 1 + i \frac{\hbar}{2 \tau} \frac{\left| \Delta_0 \right|^2}{(s^2 - \left| \Delta_0 \right|^2)^{3/2}} = 0.$$

The solution for $s$ results in the gap being given by

$$E_g = \Delta_0 \left[ 1 - \left( \frac{\hbar}{2 \tau \Delta_0} \right)^{3/2} \right].$$

The gap is reduced by increasing the impurity scattering rate, and the gap first falls to zero when $\frac{\hbar}{2 \tau} = \Delta_0$ in the regime where $\Delta_0$ and $T_c$ are still finite. For larger impurity scattering rates, the BW phase is gapless.

For the ABM phase, where $\tilde{d}(k) = \hat{z} \Delta_0 \sin \theta e^{i \phi}$, one finds

$$s - E = i \frac{\hbar}{4 \tau \Delta_0} s \ln \left( \frac{s + \Delta_0}{s - \Delta_0} \right).$$

(10.109)
The density of states at $E = 0$ is found from the solution for $s(0)$

\[ s(0) = 0 \quad , \quad \text{for} \quad \left( \frac{\hbar}{4 \tau \Delta_0} \right) < \frac{1}{\pi} \]

\[ s(0) = i \Delta_0 \cot \left( \frac{2 \tau \Delta_0}{\hbar} \right) \quad , \quad \text{for} \quad \left( \frac{\hbar}{4 \tau \Delta_0} \right) > \frac{1}{\pi} \quad (10.110) \]

which shows the transition to a gapless phase for large impurity scattering rates. In the gapless phase, the zero energy quasi–particle density of states is given by

\[ \rho_{ABM}(0) = -\frac{2 \tau \Delta_0}{\hbar} \rho(\mu) \cot \left( \frac{2 \tau \Delta_0}{\hbar} \right) \quad \text{for} \quad \left( \frac{\hbar}{4 \tau \Delta_0} \right) > \frac{1}{\pi} . \quad (10.111) \]

For finite $E$, the equation for $s(E)$ can be solved iteratively in powers of $E$. For low impurity scattering rates, one finds the solution

\[ s = \frac{E}{1 - \left( \frac{\pi \hbar}{4 \tau \Delta_0} \right)} + i \frac{E^2 \hbar}{2 \tau \Delta_0^2} \left[ 1 - \left( \frac{\pi \hbar}{4 \tau \Delta_0} \right)^3 \right] + \ldots \quad (10.112) \]

which yields a density of states which varies as $E^2$ for low energies

\[ \rho_{ABM}(E) = \rho(\mu) \left( \frac{E}{\Delta_0} \right)^2 \left[ 1 - \left( \frac{\pi \hbar}{4 \tau \Delta_0} \right)^3 \right] + \ldots \quad (10.113) \]

due to isolated point nodes. The coefficient of the $E^2$ term in the quasi–particle density of states diverges at a critical value of the scattering rate

\[ 1 = \left( \frac{\pi \hbar}{4 \tau \Delta_0} \right) \quad (10.114) \]

at which point the ABM phase becomes gapless as the isolated nodes grow into regions of finite area.

For the polar phase, a similar analysis yields

\[ s - E = i \left( \frac{\hbar}{2 \tau \Delta_0} \right) s \arcsin \left( \Delta_0 s \right) . \quad (10.115) \]

This has the solution at $E = 0$ which is always given by

\[ s(0) = i \frac{\Delta_0}{\sinh \left( \frac{2 \tau \Delta_0}{\hbar} \right)} \quad (10.116) \]
and hence, the quasi–particle density of states is
\[
\rho_{p} (0) = \rho (\mu) \frac{\left( \frac{2 \tau \Delta_{0}}{\hbar} \right)}{\sinh \left( \frac{2 \tau \Delta_{0}}{\hbar} \right)}.
\] (10.117)

This shows that the critical impurity scattering rate for producing a gapless phase is zero. Thus, the line nodes grow into regions of finite area, and the superconductivity becomes gapless, even for the slightest concentration of impurities. The calculated quasi–particle density of states for these three \( p \)–wave states are shown in Fig. 10.25, for various impurity scattering rates.

The above analysis were based on the assumption that the impurity scattering potential is sufficiently weak so that the Born approximation is adequate. However, in heavy–fermion systems, the large value of the quasi–particle density of states invalidates the above approach, as was first pointed out by Pethick and Pines [156]. The increased strength of the scattering mechanism can lead to marked modifications of the low–energy variation of the quasi–particle density of states. Within the limit of low impurity concentration, one can sum the series of multiple scattering processes involving the same impurity to yield the T–matrix result for the impurity self–energy
\[
\Sigma (k; i\hbar \omega_n) = c_0 \sum_{p} U_0 \rho_4 G(p; i\hbar \omega_n) \left[ 1 - \sum_{p'} U_0 \rho_4 G(p'; i\hbar \omega_n) \right]^{-1} \rho_4 U_0
\] (10.118)

A dimensionless measure of the strength of the scattering from a single impurity is given by the normal state phase shift \( \delta_0 \), which is given by
\[
\tan \delta_0 = - \pi U_0 \rho (\mu)
\] (10.119)

for the case of low–energy scattering and electron–hole symmetry. The limit of resonant scattering (\( \delta_0 = \pm \frac{\pi}{2} \)) can be treated similarly to the weak scattering results, and the quasi–particle density of states is given by
\[
\rho_{qp}(E) = \rho (\mu) \Re \left[ \int \frac{d \Omega_k}{4 \pi} \frac{s}{\sqrt{s^2 - |d(k)|^2}} \right],
\] (10.120)

where \( s(E) \) is found from
\[
\frac{c_0}{\pi \rho (\mu)} \frac{i}{s - E} = \int \frac{d \Omega_k}{4 \pi} \frac{s}{\sqrt{s^2 - |d(k)|^2}}.
\] (10.121)
Fig. 10.25. The quasi–particle density of states for various phases of \( p \)-wave superconductors, and different strengths of the impurity scattering rate \( \Gamma \). The impurity scattering rate is evaluated in the Born approximation [After Ueda and Rice (1985), [154]]
In this limit, the low–energy density of states is different from the density of states found in the Born approximation. For example, the consistency relation for the ABM state can be solved at $E = 0$ to yield

$$s(0) = i \frac{1}{\pi} \sqrt{\frac{c_0}{2 \rho(\mu) \Delta_0}}$$

$$for \ 1 \gg |s(0)|.$$  \ (10.122)

Thus, the quasi–particle density of states is gapless for arbitrarily small concentrations of impurities and has the value

$$\rho_{ABM}(0) = \rho(\mu) \sqrt{\frac{c_0}{2 \rho(\mu) \Delta_0}}$$  \ (10.123)

which is a non–analytic function of the concentration, $c_0$. This result for resonant scattering is in contrast to the Born approximation result for the ABM phase where there is a finite critical value of the impurity scattering rate. Furthermore, as shown in Fig. 10.26, for resonant impurity scattering, the ABM and polar states have low–energy maxima in the quasi–particle density of states [157]. As the order parameter is traceless, the balance between the diagonal and off–diagonal self–energy terms is also destroyed in the anisotropic singlet pairing phases. Generally, the different scaling behavior of the frequency and gap destroys the invariance of the quasi–particle density of states and leads to an increase in the number of low–energy states. Thereby, the simple power law dependences of the quasi–particle density of states and the concomitant power law dependences of the low temperature thermodynamic properties that are expected from the symmetry of the order parameter are spoiled. However, the power law dependences expected from the quasi–particle excitation spectrum could also be spoilt by the effect of collective excitations. The manner in which collective excitations affect the spectrum of excitations in the normal state and in the superconducting state is much less well understood.

### 10.3 Properties of the Normal State

Many properties of the normal state of heavy–fermion materials definitively show the existence of a characteristic temperature that marks the crossover from the high temperature local moment phase to the low temperature non–magnetic phase. In the literature on Ce heavy–fermion materials, this characteristic temperature is often referred to as the Kondo temperature, $T_K$, since the high temperature phase shows properties characteristic of a site independent local moments that spin–flip scatter with the conduction electrons. In this high temperature regime, the local moments can be viewed in terms of the single–impurity Anderson model [158]. In the Anderson model, the local $f$ states are broadened by the mixing with the conduction band...
density of states. The width of the virtual bound state $\Delta$ is approximately given by the Fermi–Golden rule expression

$$\Delta = \pi \rho(\mu) | V |^2,$$

(10.124)

where $\rho(\mu)$ is the conduction band density of states at the Fermi energy, and $V$ is the hybridization matrix element. An on–site local Coulomb interaction $U$ tends to prevent multiple occupancy of the $f$ level. When $U > \Delta$ and when
Fig. 10.27. The density of states of the single–impurity Anderson model, as calculated in the Hartree–Fock approximation. The density of states is composed of the sum of the conduction band contribution and a contribution from the $f$ state on the impurity. In the mixed valent limit, shown in upper figure, the virtual bound state is unpolarized. The virtual bound state is located at the energy $E_f + U n_f/2$. In the Kondo limit where the local moment is present, the virtual bound state is spin split, as shown in lower figure. [After Anderson (1961), [158]]

the $f$ level is almost singly occupied, a Hartree–Fock treatment [158] yields a solution which possesses a local magnetic moment. In the local moment or Kondo regime, the impurity $f$ density of states is spin–split and broadened, as is shown in Fig. 10.27. However, this solution is only approximate since spin–rotational invariance has been broken locally, and the residual interactions between the local moment and the conduction electrons are expected to flip the local moment and hence, restore the broken symmetry. These residual interactions were investigated by Schrieffer and Wolf [159], who mapped the
local moment limit of the single–impurity Anderson model onto the single–impurity Kondo model. In the single–impurity Kondo model [160], the repeated spin–flip scattering between the local moment and the conduction electrons results in the formation of a singlet bound state. The properties of the Kondo model show scaling with the energy of the bound state which is $k_B T_K$. The Kondo temperature for a spin one–half impurity is estimated to be of the order of

$$k_B T_K \sim \rho(\mu)^{-1} \exp \left[ \frac{\pi (E_f - \mu)}{2 \Delta} \right],$$

(10.125)

where $E_f$ is the energy of a single electron in the $f$ state of the isolated impurity. Due to the presence of the exponential factor, the Kondo temperature is expected to be much smaller than $\Delta$. For temperatures above $T_K$, the bound state is thermally depopulated, and the high temperature properties may be adequately described by low order perturbation expansions [161]. However, as the temperature is decreased below the Kondo temperature, the resonant nature of the scattering increases and weak–coupling perturbation approximation fails, since the model scales to a strong–coupling fixed point [162,163]. Near this fixed point, the properties scale with $T/T_K$ and are qualitatively described by a gas of non–interacting quasi–particles residing in a narrow virtual bound state of width $k_B T_K$ located near the Fermi energy (see Fig. 10.28). The exact Bethe–Ansatz solution [164–166] of the model shows that the low temperature properties are those of a local Fermi liquid. In the local Fermi liquid, the low temperature susceptibility is enhanced relative to the linear $T$ coefficient of the specific heat by a factor that depends on the degeneracy, $N$, of the ground state magnetic configuration. For large degeneracies, the relative enhancement or Wilson ratio is simply $N/(N - 1)$.

Although the Wilson ratio and the scaling property of the Kondo impurity model are in reasonable agreement with experimental results on dilute Ce systems, Nozières has questioned whether the results of the simple Kondo model can be directly applied to concentrated Ce compounds [167]. In particular, in the Kondo model the screening of a local moment only involves electrons within $k_B T_K$ of the Fermi–level. For a concentrated compound in which the moments on each $f$ ion are screened by a number of conduction electrons localized around each of them, the number of conduction electrons required for screening is far greater than the number $k_B T_K \rho(\mu)$ allowed for by the solution of the single impurity model. If instead, one assumes that the screening electrons remain itinerant and only form a resonance instead of a bound state, the spin–flip interaction of the conduction electrons with the local moments may still produce a non–magnetic state in which the local moments are slowly fluctuating. That is, Nozières argument does not apply if the conduction electrons responsible for the screening remain itinerant [168]. In this case, one must abandon the purely local description at sufficiently low temperatures.
It is more likely that the Kondo paradigm contains the generic physics of local electronic correlations observed in the heavy-fermion materials. This has lent credence by the recent discovery, based on the infinite dimensional limit \( d \to \infty \), that strongly correlated metals can have physical properties which qualitatively resemble those of localized magnetic impurities [169–171]. The limit \( d \to \infty \) of most many-body models is usually exactly soluble via mean-field theory and can be scaled such that it can be exactly mapped onto a non-trivial effective local impurity model. In the resulting dynamical mean-field theory, the local fluctuations on the neighboring lattice sites are treated as being governed by an effective single-impurity Anderson model in which the hybridization to the conduction electron density of states has to be determined self-consistently [172, 173]. This theoretical approach is more promising than that of the single impurity Kondo model, as it decouples the temperature scale of the resonant magnetic scattering in the high temperature regime, and the temperature scale below which the low temperature Fermi liquid forms [174]. In addition to the questions posed by Noziéres, it is quite unclear how the \( U \) compounds could be directly described by simple Kondo impurity models in which the \( 5f \) states are assigned as belonging to a unique magnetic configurations. It seems more likely that the \( U \) systems may be described by more general many-body models such as multi-band Hubbard models, which may also be described by dynamical mean-field theory. The application of dynamical mean-field theory to heavy-fermion systems is limited by its failure to describe non-local correlations. As dynamical mean-field theory omits the effect of non-local spin-fluctuations, and as quantum
critical points occur when the non–local magnetic correlations dominate over the local spin–fluctuations [89], dynamical mean–field theory is expected to be inadequate close to quantum critical points.

For some heavy–fermion compounds, the characteristic temperatures $T_K$ inferred from thermodynamic, transport, magnetic and other spectroscopic probes, are quite consistent. However, even for these systems, the low temperature thermodynamic properties do show the existence of other low–energy scales that are often attributed either to Fermi liquid formation or the onset of spatial coherence or spatial magnetic correlations. In the quantum critical point description, this coherence temperature is identified as the cross–over temperature at which the physics of the quantum critical point gives way to the physics of the Fermi liquid fixed point [176, 177]. In a phase space that is extended, as for instance when pressure is applied, the line of cross–over points is experimentally accessible since physical quantities should exhibit extrema on parallel lines. The phenomenon of coherence is most clearly manifested in transport phenomena, though it does also show up directly in high resolution spectroscopic measurements on single crystals [177]. The phenomenon of coherence falls beyond the scope of the exactly soluble single–impurity Kondo models or dynamical mean–field theory and, therefore, still lacks an adequate theoretical description.

10.3.1 Thermodynamic Properties

The Specific Heat

The low temperature specific heats of the normal state phase of heavy–fermion systems are dramatically different from ordinary metals. The extrapolated value of the ratio of the specific heat to the temperature

$$\lim_{T \to 0} \frac{C(T)}{T} = \gamma$$

(10.126)

can be of the order of 1 J / mole K$^2$, which is 1000 times larger than the corresponding ratio for Cu. In many heavy–fermion systems, notably UBe$_{13}$, CeCu$_2$Si$_2$, CeAl$_4$ and CeCu$_6$, the ratio $C(T)/T$ shows an increase with decreasing temperatures, at low temperatures, and shows signs of saturation. For UBe$_{13}$ and CeAl$_3$ the upturn starts at a scale of the order of 10 K. The heat capacity of UBe$_{13}$ is shown in Fig. 10.29. The large magnitudes of the extrapolated specific heat coefficients $\gamma$ are attributed in part to the flat quasi–particle dispersion relation arising from the small hybridization between the $f$ orbitals and the states on the ligand atoms and in part due to the average of the quasi–particle mass enhancement, $Z_k$. The assignment of the large value of the $\gamma$ coefficient as being due to enhanced quasi–particles is found to be consistent with de Haas–van Alphen measurements. For UPt$_3$ and UAl$_2$, the specific heat has the form

$$C(T) = \gamma T + \delta T^3 \ln T + \beta T^3$$

(10.127)
Fig. 10.29. The specific heat in the normal state of UBe$_{13}$ divided by temperature as a function of $T^2$. [After Ott et al. (1983) [4]]. Note the upturn at low temperatures and the large extrapolated value at $T = 0$ as compared to the value of 0.07 mJ/mole/K$^2$ for Cu

for temperatures up to 20 K. The low temperature specific heat of UPt$_3$ and the fit to this form are shown in Fig. 10.30. The above form and the sign of $\delta$ are compatible with a Fermi liquid that exhibits large amplitude, long wavelength, collective fluctuations such as ferromagnetic spin–fluctuations [89,90,95,96]. The values of the coefficients $\beta$ are also quite large compared with values expected from phonon contributions in normal metals and probably could also have a significant electronic component. The entropies calculated from the enhanced low temperature specific heats have values comparable to those of a disordered set of independent moments on the $f$ ions, suggesting a magnetic origin of the enhancement. This conclusion is strengthened for UAl$_2$ by the finding [179,180] that an applied magnetic field actually suppresses the low temperature upturn in $C/T$.

An unusual feature of the specific heat of some heavy–fermion systems is that they seem to indicate that the fluctuations are of a local character and reside mainly on the $f$ ions. For example, on substituting La for Ce in CeCu$_6$, the temperature dependence of the specific heat of Ce$_x$La$_{1-x}$Cu$_6$ per Ce ion is independent of $x$, for $1 > x > 0.5$, indicating that the large specific heat of this Ce compound is dominated by local processes [181]. A similar conclusion was previously drawn from dilution studies of CePb$_3$ [182], where it was found that the properties simply scale with the Ce concentration. The specific heats per mole Ce of diluted CePb$_3$ and CeCu$_6$ are shown in Fig. 10.31. This type of scaling behavior should be contrasted with the behavior found in dilution studies of CeCu$_2$Si$_2$, CeAl$_3$ and UBe$_{13}$. In stoichiometric CeAl$_3$, the $C/T$ ratio shows a small maximum around $T = 0.3$K [183], and on doping
Fig. 10.30. The low temperature specific-heat ratio \( C(T)/T \) versus \( T^2 \) for \( UPt_3 \). The solid line is a fit to \( C(T) = \gamma T + \delta T^3 \ln T \). The dashed line is a fit to \( \gamma T + \beta T^3 + \delta/T \). [After Stewart et al. (1984), [6]]

substitutionally for Ce with La, the peak moves up to higher temperatures. However, the Kondo temperature decreases with doping [184]. Calculations based on single impurity models show that the low temperature peak is not simply due to the Kondo effect in the presence of crystal fields [185, 186]. Therefore, it has been speculated that the peak is either due to the onset of magnetic correlations or is a manifestation of structure in the quasi-particle density of states caused by the coherence of the lattice.

There exists a similar low temperature peak in the specific heat of \( UBe_{13} \) near \( T = 2K \) which is suppressed and moves towards lower temperature on substituting 3 percent of U by Th [187]. Substitutional doping on the U sites of \( UBe_{13} \) by a few percent of impurities leads to a rapid decrease in the \( \gamma \) value. The introduction of roughly 3% concentration of impurities leads to a depression of \( \gamma \) by roughly 30%. These studies suggest that the value of \( \gamma \) crucially depends on the U – Be separation. Stoichiometric \( CeCu_2Si_2 \) seems to be on the critical phase boundary between a phase that exhibits magnetic correlations at low temperatures, the \( A \) phase and a phase that superconducts at low temperatures, the \( S \) phase. A generalized phase diagram of \( CeCu_2Si_2 \) is shown in Fig. 10.32. The \( A \) and \( S \) phases seem to coexist in stoichiometric
Fig. 10.31. (a) The excess specific heat per mole Ce, $\Delta C$ versus $T^2$ for $\text{Ce}_{1-x}\text{La}_x\text{Pb}_3$ samples with $x = 0.0, 0.2, 0.4, 0.6$ and $0.8$. Insert: The total specific heat per molar formula unit divided by $T$ for the same samples. [After Lin et al. (1987), [182]]. (b) The specific heat per mole Ce for $\text{Ce}_x \text{La}_{1-x} \text{Cu}_6$ with $x = 1, 0.8$ and $0.5$, plotted versus $T$. [After Ōnuki and Komatsubara (1987), [181]]
Fig. 10.32. A schematic phase diagram for CeCu$_2$Si$_2$ at zero field, indicating the existence ranges for a spin density wave–like phase (A), superconductivity (S), and the coexistence ranges (A+S). The abscissa is an effective coupling constant $g$ which is proportional to $x$ in CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ or to the composition in homogeneous CeCu$_2$Si$_2$. [After Gegenwart et al. (1998), [192]]

single crystals [188]. In this case, altering the composition can result in the stabilization of the separate phases [189, 190]. The A phase shows a specific heat due to heavy quasi–particles perhaps including a $T^3 \ln T$ contribution arising from ferromagnetic spin–fluctuations [191]. In the presence of applied magnetic fields sufficiently large to suppress the superconductivity, the S phase appears and has a non–Fermi–liquid like temperature dependence of the specific heat [192]

$$\frac{C}{T} = \gamma_0 - A T^{1/2}. \quad (10.128)$$

This non–analytic temperature variation indicates that the material is either close to a quantum critical point in which non–local correlations are developing, or that there is a significant amount of local disorder as has been inferred from neutron measurements of the nuclear pair distribution function [193].

**The Magnetic Susceptibility**

The magnetic susceptibilities of heavy–fermion systems show temperature driven cross–overs between forms reminiscent of local moments and low temperature Pauli–like susceptibilities. This is illustrated in Fig. 10.33, which shows the temperature dependence of the susceptibilities for UBe$_{13}$ and CeAl$_3$. At high temperatures, the susceptibilities can be fit by the form

$$\chi(T) = n \frac{\mu_{eff}^2}{3 k_B (T - \Theta)}, \quad (10.129)$$
Fig. 10.33. The temperature dependence of the magnetic susceptibility $\chi(T)$ for UBe$_{13}$ and CeAl$_3$ plotted as $\chi^{-1}(T)$. The effective moments and Curie–Weiss temperature obtained from high temperature fits are also shown. At low temperatures, the temperature variation of $\chi(T)$ for CeAl$_3$ weakens and becomes Pauli–paramagnetic, as shown in the inset.

where $\mu_{\text{eff}}$ is the size of the effective magnetic moment, $n$ is the density of local moments, and $\Theta$ is the Curie–Weiss temperature. The values of the effective moment $\mu_{\text{eff}}$ are nearly that of the free ionic moments, and the values of the Curie–Weiss temperature $\Theta$ are usually negative, suggesting antiferromagnetic interactions between the local moments.

At lower temperatures, the susceptibilities cross–over to Pauli–paramagnetic susceptibilities that show large enhancements similar to those of the specific heat $\gamma$ coefficients. The cross–over from Curie–Weiss like to Pauli–paramagnetic like susceptibilities seems to occur at higher temperatures than the temperatures at which the $C/T$ ratios build up [194,195]. The magnitudes
Table 10.8. High Temperature Properties of the Normal State. Anisotropic properties of crystals are given along the principal directions in the form of “a/b/c”.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Theta$ (K)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>$\rho(T = 300K)$ ($\mu\Omega$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCu$_5$</td>
<td>284</td>
<td>3.52</td>
<td>286</td>
</tr>
<tr>
<td>UAl$_2$</td>
<td>245</td>
<td>3.1</td>
<td>190</td>
</tr>
<tr>
<td>UPt$_3$</td>
<td>50 / 170</td>
<td>2.5 / 2.34</td>
<td>230 / 135</td>
</tr>
<tr>
<td>U$_2$Zn$_17$</td>
<td>105</td>
<td>3.3</td>
<td>110</td>
</tr>
<tr>
<td>URu$_2$Si$_2$</td>
<td>65</td>
<td>3.51</td>
<td>324 / 169</td>
</tr>
<tr>
<td>UBe$_{13}$</td>
<td>53</td>
<td>3.1</td>
<td>107</td>
</tr>
<tr>
<td>UPd$_2$Al$_3$</td>
<td>47</td>
<td>3.2</td>
<td>140 / 200</td>
</tr>
<tr>
<td>UCD$_{11}$</td>
<td>23</td>
<td>3.45</td>
<td>80</td>
</tr>
<tr>
<td>UGe$_2$</td>
<td>- 34</td>
<td>2.7</td>
<td>156</td>
</tr>
<tr>
<td>CeCu$_2$Si$_2$</td>
<td>140</td>
<td>2.68</td>
<td>90</td>
</tr>
<tr>
<td>CeCu$_6$</td>
<td>59 / 59 / 8</td>
<td>2.6 / 2.67 / 2.46</td>
<td>70</td>
</tr>
<tr>
<td>CeAl$_3$</td>
<td>46</td>
<td>2.63</td>
<td>65</td>
</tr>
</tbody>
</table>

of the measured $\gamma$ and $\chi(0)$ can be compared indirectly by using the model of non–interacting electrons. For the gas of non–interacting electrons, the Pauli–susceptibility is given by

$$\chi(0) = 2 \mu_B^2 \rho(\mu),$$

(10.130)

where $\rho(\mu)$ is the density of states, per spin, at the Fermi energy, and the specific heat coefficient is given by

$$\gamma = 2 \frac{\pi^2}{3} k_B^2 \rho(\mu).$$

(10.131)

Therefore, a plot of $\gamma$ versus $\chi(0)$ for hypothetical non–interacting electron systems should yield a straight line with slope given by

$$\frac{\pi^2}{3} \left( \frac{k_B}{\mu_B} \right)^2.$$

(10.132)

As shown by Fisk et al. [196] (see Fig. 10.34), the heavy–fermion systems have $\gamma$ and $\chi(0)$ values that lie close to the same line. Therefore, as the Wilson ratio is close to unity, this indicates that the enhancements of the susceptibilities have similar magnitudes to the specific heat enhancements.
From a Fermi liquid point of view, one would expect that the uniform static susceptibility should show an enhancement, $S$, given by

$$S = \frac{m^*/m_b}{1 + F_{0}^a}, \quad (10.133)$$

where $F_{0}^a$ is the spin antisymmetric interaction between a pair of quasi-particles with angular momentum $l = 0$. However, the specific heat is just enhanced by the factor

$$m^*/m_b. \quad (10.134)$$

Thus, the $\chi$ to $\gamma$ ratio yields information about the spin-dependent interaction between the quasi-particles. In most Ce compounds, both enhancements seem to be due to single-site processes. This can be seen by inspection of the susceptibility of Ce$_x$La$_{1-x}$Cu$_6$ per Ce ion, which is independent of $x$ in the range $1 > x > 0.1$. The susceptibilities of Ce$_x$La$_{1-x}$Cu$_6$ and Ce$_x$La$_{1-x}$Pb$_3$ are shown in Fig. 10.35. The similarity of the curves suggests that the large susceptibility, like the large specific heat, is dominated by local processes involving the $f$ electrons. Since the spin–orbit split ground state of the Ce$^{3+}$ ion corresponds to $J = 5/2$ and degeneracy of 6, the ratio of the susceptibility to $\gamma$ term predicted by the single-site Kondo model should be very similar to
the ratio for non–interacting electrons. On the other hand, in UBe$_{13}$ doped substitutionally on the U sites [197], the susceptibility seems to scale linearly with the number of U atoms, while the $\gamma$ coefficient per U atom is rapidly reduced by dilution. This suggests that an appreciable fraction of the mass enhancement in UBe$_{13}$ is not due to a single–site magnetic Kondo process. A similar conclusion has been drawn from dilution studies of UPt$_3$ [198], which show that dilution can result in the suppression of the specific heat by up to 50% of the stoichiometric value while the uniform static susceptibility is barely affected. These conclusions are consistent with measurements of the de Haas – van Alphen oscillations on a number of U and Ce compounds, which show that the quasi–particles are itinerant and form part of the Fermi surface, albeit with a very small dispersion of the bands.

**de Haas–van Alphen oscillations**

Measurements of the magnetization in high fields and at low temperatures show oscillations as a function of the inverse field. The presence of the oscillations has long been held as an indicator that the quasi–particles are itinerant, form part of the Fermi surface, and are long lived. The oscillations are due to the existence of Landau peaks in the density of states, which are a consequence of the quantized orbital motion of the quasi–particles in the presence of an applied field. As the applied field is increased, the energy separation between consecutive Landau peaks increases linearly with the field, and the oscillations occur as the peaks in the density of states move through the Fermi energy. The fundamental periods of the oscillations are related to the extremal cross–sectional areas of the Fermi surface perpendicular to the applied field. For non–interacting electrons, the fundamental oscillation stemming from each electron orbit around an extremal area is governed by the Lifschitz – Kosevich formula

$$M_z = A \cos \left( \frac{hc}{eH_z} S + \phi \right),$$

where $S$ is the extremal area of $k$ space enclosed by the quasi–particle orbiting around the Fermi surface, and $\phi$ is a phase reflecting the Zeeman splitting between the bands of different spins. The amplitude of the oscillations, $A$, is given by

$$A \sim V \frac{k_BT}{2\pi^2} \frac{S}{\sqrt{\frac{e}{hcH_z}}} \exp \left[ -\frac{2\pi^2 m_b e}{\tau eH_z} \right] \cosh \left[ \frac{2\pi^2 m_b e k_BT}{hcH_z} \right],$$

where $\tau$ is the lifetime due to scattering processes and $m_b$ is the effective mass deduced from the dispersion relation of the non–interacting electrons at the Fermi surface. The scattering rate, $1/\tau$, is usually introduced in an ad–hoc manner. The contribution from each extremal area contributes to the
Fig. 10.35. (a) The magnetic susceptibility per mole Ce, $\chi(T)$ versus $T$ for Ce$_{1-x}$La$_x$Pb$_3$ samples with $x = 0, 0.2, 0.4, 0.6$ and $0.8$. Insert: The total susceptibility per molar formula unit for the same samples. [After Lin et al. (1987), [182]].

(b) The magnetic susceptibility per mole formula unit for Ce$_x$La$_{1-x}$Cu$_6$, plotted versus $T$. [After Ōnuki and Komatsubara (1987), [181]]

signal with the weight given by

$$\sqrt{\frac{2\pi}{|\frac{\partial^2 S}{\partial k_z^2}|}},$$  \hspace{1cm} (10.137)

where $k_z$ is the component of the wave-vector parallel to the field. This factor expresses the weight of an extremal cross-section relative to that of an extremal section of a spherical Fermi surface of the same size, $S$. Since Fermi surfaces are often multi-sheeted, the measured areas are typically compared
with the results of electronic structure calculations. For most simple metals, the experimentally determined areas are usually in excellent agreement with the LDA calculations. Since the oscillations originate from the Landau peaks in the density of states passing through the Fermi energy, broadening, either due to the Fermi function or from the effect of impurity scattering on the Landau peaks, is expected to wash out the oscillations. Therefore, one expects that the oscillations should only be measurable at extremely low temperatures \( T < 1 \, \text{K} \), for high fields, and for very high quality samples having very low residual resistivities.

The Lifschitz–Kosevich formula must be modified when the effect of electron–electron interactions are introduced. First, the spin–splitting phase factor \( \phi \) may be exchange enhanced and may become field–dependent [199]. Phenomenologically, one is also led to expect that the scattering rate should be identified with the imaginary part of the self–energy evaluated on the Fermi surface and that the real part of the self–energy may also be expected to appear as an addition to the imaginary part. In the thermal average which is performed by transforming to a sum over Matsubara frequencies \( \omega_n \), the real part of the self–energy contains a term proportional to \( 1 - Z(0) \omega_n \), and therefore, produces a correction of order \( \pi k_B T \). In the small \( H/T \) limit, the additional term originating from the real part of the self–energy can be combined with the \( k_B T \) dependence in the argument of the cosech term in the non–interacting formulae, thereby replacing the band mass \( m_b \) by the quasi–particle mass \( m^* \). Thus, the temperature dependence of the amplitude of the oscillations can be used to deduce the quasi–particle effective masses. As the linear \( T \) term in the specific heat–capacity is related to the average of the quasi–particle masses on the Fermi surface, one may be able to compare the average of the quasi–particle masses observed in de Haas–van Alphen experiments with the specific heat. However, in attempting to make this comparison, it is important to note that some portions of the Fermi surface may not have been observed in the de Haas–van Alphen experiments. As can be seen from Eq. (10.136), the amplitudes of the heavier branches are expected to be quite small and may easily be missed. Also, in the case where the \( \gamma \) coefficient depends on the magnitude of the applied field, as it should if the quasi–particle mass enhancements are of magnetic origin, the average quasi–particle mass should be compared with the specific heat measured under comparable fields. It should be noted that the amplitude factor contains the ratio of the quasi–particle mass to the quasi–particle lifetime so, if the mass enhancements arise from a local process, the quasi–particle mass enhancement factor should cancel with the enhancement of the quasi–particle lifetime. This cancellation occurs much in the same way as the cancellation of the enhancements in the residual resistivity \( \rho(0) \) that occurs when the self–energy is \( k \) independent. This implies that the impurity scattering should not be significantly more effective in reducing the amplitude of the oscillations than in metals with comparable density of states.
The de Haas–van Alphen oscillations were observed in measurements on CeCu$_6$, CeCu$_2$Si$_2$, UCd$_{11}$, UPt$_3$, UPd$_2$Al$_3$, URu$_2$Si$_2$ and CeRu$_2$Si$_2$ for temperatures between 200 and 100 mK and fields up to 18 T. Despite many valiant attempts, measurements on UBe$_{13}$ have failed to yield de Haas van–Alphen oscillations [200]. In most of these materials, sheets of the Fermi surface with large effective masses have been found. The extremal areas inferred for UPt$_3$ are in good agreement with the Fermi surface geometry found from electronic structure calculations [201,202]. The effective masses inferred from the amplitude can be factors of 10 to 30 times larger than those found in LDA band structure calculations [203,204], and the heavy masses found range from 25 $m_e$ to 200 $m_e$. This suggests that the quasi–particle mass enhancements due to electron–electron interactions, are extremely large. The Fermi surface average of the observed effective masses produces a quasi–particle density of states that is in rough agreement with the $\gamma$ value of UPt$_3$. Whereas in UPt$_3$ the quasi–particles at the Fermi surface have large effective masses, the effective masses found in CeCu$_6$ are smaller [207] and are in the range of 6 to 80 $m_e$. However, as the specific heat of CeCu$_6$ is appreciably larger than that of UPt$_3$, one suspects that the bands with heavier masses were not observed. This situation also seems to be definitely the case for CeCu$_2$Si$_2$ in which only small masses of 4 to 6 $m_e$ have been observed [205]. The observation of the heavy mass sheets of the Fermi surface in UPt$_3$, but not in CeCu$_6$ and CeCu$_2$Si$_2$, is probably due to the higher quality of the UPt$_3$ samples. Also, part of the discrepancy between the de Haas – van Alphen effective masses and the specific heat of CeCu$_6$ measured in zero field [206,207] is accounted for, if the field dependence of the specific heat is considered [208,209]. The decrease of the effective mass with applied magnetic field is taken as an indication that spin–flip excitations are responsible for part of the mass renormalizations, and that application of the field quenches the spin–flip scattering processes. The lack of agreement between the specific heat and de Haas – van Alphen effective masses in URu$_2$Si$_2$ is very notable in that the only effective masses that have been found, so far, are in the range of 15 to 25 $m_e$, and these only yield about 16 percent of the total $\gamma$ value [210,211]. Likewise for UCd$_{11}$ [214], the only effective masses observed are only in the range of 2 to 11 $m_e$. As previously mentioned, the difficulty of observing heavy quasi–particle mass branches of the Fermi surface is due to the exponentially small amplitudes of their oscillations. However, both light and heavy quasi–particle masses can be found in the same compound such as in CeRu$_2$Si$_2$, where the observed masses are in the range of 1 to 120 $m_e$ [215].

Some heavy–fermion materials undergo meta–magnetic like transitions at high fields in which the magnetizations undergo rapid change with respect to magnetic field at a critical value of the field $H_m$. The meta–magnetic transitions become sharper at lower temperatures. These highly non–linear susceptibilities indicate either that the systems are on the verge of undergoing
an instability to a magnetically ordered phase \(^7\) or that a spin–split branch of quasi–particles crosses the Fermi surface. For example, URu\(_2\)Si\(_2\) may undergo as many as three transitions, located at \(H_{m1} = 35.9\) T, \(H_{m2} = 36.1\) T and \(H_{m3} = 39.7\) T. The three transitions in URu\(_2\)Si\(_2\) have been observed in transport properties [216] as well as in the magnetization [267]. UPt\(_3\) has a meta–magnetic transition at \(H_m = 20\) T while \(H_m = 18\) T for UPd\(_2\)Al\(_3\); \(H_m = 8\) T for CeRu\(_2\)Si\(_2\) and a very much weaker meta–magnetic transition occurs in CeCu\(_6\) at a critical field of \(H_m = 2\) T. Above these fields, the effective masses rapidly decrease with increasing field [218,219]. For example, in UPd\(_2\)Al\(_3\), the effective masses found below \(H_m = 18\) T are as large as 45 \(m_e\) [220], but for fields above \(H_m\), the effective masses found are 31 and 5.4 free electron masses [221].

De Haas – van Alphen oscillations have also been observed in the mixed states of type II superconductors such as NbSe\(_2\) [222], Nb\(_3\)Sn, V\(_3\)Si [223] and YNi\(_2\)B\(_2\)C [224]. This effect is probably due to the existence of unpaired quasi–particle particles which can be quantized into Landau levels similar to the manner in which the quasi–particles in the normal state are quantized into Landau levels. De Haas – van Alphen measurements have been performed in the superconducting states of UPd\(_2\)Al\(_3\) and URu\(_2\)Si\(_2\), and oscillations were observed to persist until the strength of the applied field was reduced substantially below \(H_{c2}\). Since the estimated diameters of the cyclotron orbits are factors of 10 greater than the vortex lattice spacing, the unpaired quasi–particles apparently must traverse through the superconducting regions. The frequencies of the oscillations remain unchanged in the superconducting state, however, the quasi–particle masses and scattering rates inferred from a Fermi liquid like analysis are altered. For example, the branch with mass of 5.4 \(m_e\) found in the normal state of UPd\(_2\)Al\(_3\) was also observed in the superconducting state, but the inferred effective mass was further reduced to 3.0 \(m_e\).

\(^7\) For a paramagnetic system close to a magnetic instability, one expects that the free–energy expressed as a function of the magnetization \(M\) could have a local minimum at \(M \neq 0\), in addition to the global minimum at \(M = 0\). The application of a magnetic field may cause the energy of the local minimum to be lowered, thereby stabilizing it at the critical field \(H_m\) associated with the meta–magnetic transition. The criterion for the occurrence of a meta–magnetic transition can be easily calculated for the Stoner model. In the Stoner model, the magnetization–field relation is given by

\[
M = 2\mu_0^2 H S \rho(\mu) \left[ 1 + \frac{1}{6} \left( \frac{\rho''}{\rho} - 3 \left( \frac{\rho'}{\rho} \right)^2 \mu_0^2 H^2 S^3 + \ldots \right) \right],
\]  
(10.138)

where \(S = (1 - U \rho(\mu))^{-1}\) is the Stoner enhancement factor. The terms non–linear in \(H\) can be large due to the appearance of extra powers of \(S\). The cubic term may be negative either if the density of states at the Fermi energy is close to a maximum or if it is rapidly varying. If non–linear terms in \(M\) are negative, then meta–magnetic transitions may occur at critical fields. Thus, meta–magnetic transitions may be expected to occur in the vicinity of quantum critical points.
Phenomenologically, the amplitude of oscillations could be expected to be reduced due to the decrease in the number of unpaired quasi–particles and also due to the smearing of the Fermi energy in the superconducting state. The latter phenomenon could also appear as an increase in the quasi–particle scattering rate consistent with the observations in the superconducting state of URu$_2$Si$_2$ [211]. The appearance of de Haas–van Alphen oscillations in the superconducting state is surprising since it undermines a commonly held belief that observability of the oscillations is a signature of the existence of a sharply defined Fermi surface and the long lifetime of the quasi–particles. Furthermore, it is surprising as it definitively shows that such oscillations can also be observed in non–Fermi–liquid states.

Table 10.9. Low Temperature Normal State Properties (Extrapolated to $T = 0$).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma$ (mJ mole$^{-1}$ K$^{-2}$)</th>
<th>$\chi(0)$ (10$^{-3}$ emu/mole)</th>
<th>$A$ ($\mu\Omega$ cm K$^{-2}$)</th>
<th>$\rho(0)$ ($\mu\Omega$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeAl$_3$</td>
<td>1620</td>
<td>36</td>
<td>35</td>
<td>0.77</td>
</tr>
<tr>
<td>CeCu$_6$</td>
<td>1600</td>
<td>28</td>
<td>$\sim$ 120</td>
<td>15 / 9.2 / 8.3</td>
</tr>
<tr>
<td>UE$_{11}$</td>
<td>1100</td>
<td>14.7</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>CeCu$_2$Si$_2$</td>
<td>600</td>
<td>4 / 8</td>
<td>10.7</td>
<td>4.8</td>
</tr>
<tr>
<td>UCd$_{11}$</td>
<td>840</td>
<td>39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>U$<em>2$Zn$</em>{17}$</td>
<td>500</td>
<td>19 / 24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UPt$_3$</td>
<td>360</td>
<td>8.1 / 4.4</td>
<td>1.6 / 0.61</td>
<td>0.23 / 0.59</td>
</tr>
<tr>
<td>UPd$_2$Al$_3$</td>
<td>170</td>
<td>8.1 / 2.2</td>
<td>$\sim$ 0.3</td>
<td>3.5</td>
</tr>
<tr>
<td>URu$_2$Si$_2$</td>
<td>180</td>
<td>1.5 / 4.9</td>
<td>0.17 / 0.10</td>
<td>1.27</td>
</tr>
<tr>
<td>UNi$_2$Al$_3$</td>
<td>150</td>
<td>3.3 / 2.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UAl$_2$</td>
<td>142</td>
<td>4.3</td>
<td>10.7</td>
<td>4.8</td>
</tr>
<tr>
<td>UGe$_2$</td>
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<td>-</td>
<td>$\sim$ 0.25</td>
<td>0.26</td>
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<tr>
<td>CePd$_2$Si$_2$</td>
<td>250</td>
<td>11</td>
<td>-</td>
<td>1.4</td>
</tr>
<tr>
<td>CeRh$_2$Si$_2$ (P=0)</td>
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<td>2.9 - 3.2</td>
<td>0.8</td>
<td>0.75</td>
</tr>
<tr>
<td>CeIn$_3$</td>
<td>100</td>
<td>11</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>CeRhIn$_5$ (P=0)</td>
<td>60</td>
<td>4 - 22</td>
<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>CeIrIn$_5$</td>
<td>750</td>
<td>9 - 20</td>
<td>-</td>
<td>$\sim$ 0.1</td>
</tr>
<tr>
<td>CeCoIn$_5$</td>
<td>350</td>
<td>4 - 7</td>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>

Magnetic Instabilities
Several of the heavy–fermion materials undergo instabilities to magnetically ordered states at lower temperatures. The most frequently found type of ordering is antiferromagnetic, however, ferromagnetic phases have been iden-
tified in UGe$_2$, URhGe, CeRu$_2$Ge$_2$, CeGe$_2$, and CeSi$_2$. The values of $\gamma$ found from extrapolation above the ordering temperatures are generally about a factor of 1.2 to 3 times higher than the $\gamma$ values found from extrapolating below the ordering temperatures. This indicates that the antiferromagnetic order may have produced a partial gapping of the Fermi surfaces. Exceptions to this are given by CeAl$_3$, UCu$_5$ and UPt$_3$, where the extrapolated $\gamma$ values are larger in the magnetically ordered phases. These findings are consistent with the general observation that the entropy found by integrating below the ordering temperature is about 30 percent less than entropy expected from a simple Fermi liquid picture, i.e., $\gamma$ may still be growing below $T_N$ and the Fermi liquid may have not been completely formed when $T$ has been decreased to $T_N$.

The values of the ordered moments are smaller than those associated with the free ion values. This is sometimes attributed to the screening of the $f$ moments by the conduction electrons. However, in view of Nozières arguments for Ce compounds and the existence of reduced moment ordering in U compounds, it seems apparent that the itinerant nature of the $f$ electrons is involved in the reduction of the moments. In some compounds such as CeAl$_3$ and URu$_2$Si$_2$, the magnetic ordering appears to be inhomogeneous, only occurring in a small fraction of the sample volume [225]. It seems likely that these samples are also inhomogeneous. The magnitude of the moments on the atoms in the magnetically ordered volume can be large, of the order of 0.5 $\mu_B$ per $f$ atom but the moment averaged over the sample can be as small as 0.03 $\mu_B$ per $f$ atom, as found for URu$_2$Si$_2$. It has been found [226] that in URu$_2$Si$_2$, application of pressures of up to 1.5 GPa produces an increase in the size of the ordered moment to a value of the order of 0.25 $\mu_B$ per $U$ atom but only produces a slight increase in $T_N$. The magnetic ordering shows up in the specific heat of CeAl$_3$ as a faint and sample dependent anomaly at the ordering temperature that considerably increases in magnitude on dilution. As shown in Fig. 10.36, the specific heat jump observed in stoichiometric URu$_2$Si$_2$ is quite large [20, 21]. The small magnitude of the volume averaged ordered moment in URu$_2$Si$_2$ seems inconsistent with the large value of the entropy associated with the specific heat anomaly at $T_N$. The specific heat jump is about 5.82 J/mole–K, and the entropy $\Delta S$ associated with the anomaly has a magnitude of about 0.17 $N k_B \ln 2$. On the other hand, Landau mean–field theory suggests that the magnitude of the entropy of the transition should be of the order of

$$\Delta S \sim N k_B \left( \frac{\mu_{sat}}{\mu_{eff}} \right)^2,$$

(10.139)

where $\mu_{sat}$ is the $T = 0$ saturation value of the sub–lattice magnetization; and $\mu_{eff}$ is the paramagnetic moment ($\mu_{eff} \approx 3.51 \mu_B$), as obtained from fitting the susceptibility above $T_N$ to a Curie–Weiss law. The large discrepancy between the observed and inferred magnitudes of the anomalous entropy
Fig. 10.36. The specific heat jump of the “hidden order” phase transition of URu$_2$Si$_2$. The specific heat ratio $C/T$ is plotted as a function of $T^2$. A mean field–like jump occurs at $T_N \approx 17.5$ K which is associated with the “hidden order” phase transition. [After Maple et al. (1986), [21]]

has been taken as indicating that another type of ordering occurs simultaneously with the antiferromagnetism. However, although the other type of ordering has been searched for, it has not yet been identified.

An alternate paradigm for heavy–fermion materials is provided by the model of a highly enhanced Fermi liquid close to a quantum critical point. In this picture, the large enhancements are caused by the slow, large amplitude, critical magnetic fluctuations. Due to the close proximity of the critical point, one may expect various physical quantities to obey scaling laws [73]. In this case, one expects that the properties may be expressed in terms of the $q$ dependent magnetic susceptibility $\chi(q, T)$ which expresses the response of the system to a staggered magnetic field $H(q)$. The absence of a large $\chi(0,0)/\gamma$ ratio indicates that the dominant magnetic fluctuations that occur are not localized around $q = 0$. This is consistent with the observation that most heavy–fermion systems undergo instabilities to antiferromagnetic phases. Likewise, since the transport scattering rate is dominated by processes involving large scattering angles $\theta$ due to the weighting factor of $(1 - \cos \theta)$, measurements of transport properties might also be expected to provide information on the magnitude of the wave–vectors of the magnetic fluctuations in the absence of competing instabilities and complicated multi–sheeted Fermi surfaces.
Table 10.10. Properties of the Magnetically Ordered State.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_N$ (K)</th>
<th>Ordered Moment $M$ ($\mu_B$)</th>
<th>$\gamma$ (mJ K$^{-2}$ mole $f$ ion$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeAl$_3$</td>
<td>1.6</td>
<td>-</td>
<td>1300</td>
</tr>
<tr>
<td>CeCu$_2$Si$_2$</td>
<td>0.8</td>
<td>$\sim$ 0.1</td>
<td>1000</td>
</tr>
<tr>
<td>UCd$_{11}$</td>
<td>5</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>U$<em>2$Zn$</em>{17}$</td>
<td>9.7</td>
<td>0.8</td>
<td>200</td>
</tr>
<tr>
<td>UPt$_3$</td>
<td>5.0</td>
<td>0.02</td>
<td>450</td>
</tr>
<tr>
<td>UPd$_2$Al$_3$</td>
<td>14.5</td>
<td>0.85</td>
<td>150</td>
</tr>
<tr>
<td>URu$_2$Si$_2$</td>
<td>17.5</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>UNi$_2$Al$_3$</td>
<td>4.6</td>
<td>0.24</td>
<td>120</td>
</tr>
<tr>
<td>UGe$_2$</td>
<td>$T_c(P = 1$ GPa) = 34</td>
<td>$M(P = 0) = 1.4$</td>
<td>-</td>
</tr>
<tr>
<td>CePd$_2$Si$_2$</td>
<td>10.2</td>
<td>0.7</td>
<td>250</td>
</tr>
<tr>
<td>CeRh$_2$Si$_2$</td>
<td>36</td>
<td>1.8</td>
<td>21</td>
</tr>
<tr>
<td>CeIn$_3$</td>
<td>10.2</td>
<td>0.65</td>
<td>100</td>
</tr>
<tr>
<td>CeRhIn$_5$ (P=0)</td>
<td>3.8</td>
<td>0.37</td>
<td>60</td>
</tr>
</tbody>
</table>

10.3.2 Transport Properties

**Electrical Resistivity**

The room temperature resistivities of heavy–fermion compounds are quite large, of the order of 100 $\mu\Omega$cm$^{-1}$, most probably due to spin disorder scattering. As seen in Fig. 10.37, the resistivity of some materials such as CeCu$_2$Si$_2$, CeAl$_3$, UBe$_{13}$ and U$_2$Zn$_{17}$, shows an increase with decreasing temperature. This type of temperature dependence is unusual for simple metals but is characteristic of the Kondo effect often found in materials containing isolated and disordered magnetic impurities. In this subset of heavy–fermion materials, the upturn in the resistivity follows a logarithmic temperature dependence that results from the conduction electrons resonantly spin–flip scattering from isolated magnetic impurities, as calculated in third order perturbation theory [161]. If, at high $T$, the conduction electrons are assumed to be scattered by localized moments, the conductivity is given by

$$\sigma(T) = \frac{e^2 k_F^3}{3 \pi^2 m} f^{(0)},$$

(10.140)

where

$$f^{(n)} = \int_{-\infty}^{+\infty} dE \left( - \frac{\partial f}{\partial E} \right) \frac{E^n}{Im \Sigma_c(E)}$$

(10.141)
Fig. 10.37. The temperature dependence of the electrical resistivity of the heavy fermion compounds $U_2Zn_{17}$, $CeAl_3$, $CeCu_2Si_2$ and $UBe_{13}$. The inset shows the low temperature $T^2$ variation of the resistivity found in $CeAl_3$.

and where $\Sigma_c(E)$ is the conduction electron self-energy. For independent local moments the imaginary part of the self-energy is given by

$$Im \Sigma_c(E) = \pi |V|^2 \rho_f(E,T),$$

where $\rho_f(E,T)$ is the temperature dependent $f$ density of states, and $V$ is the hybridization matrix elements. For $T < T_K$, a narrow (possibly crystal field split) Kondo resonance forms at an energy $T_K$ above $\mu$. The temperature dependent crystal–field split $\rho_f(E,T)$ expected from the single–impurity Anderson model is shown in Fig. 10.38. Thus, the resistivity is expected to reflect any crystal–field splitting that may be present. As seen in Fig. 10.39, there are two peaks in the resistivity of $CeCu_2Si_2$ [227] both of which can be attributed to spin–flip scattering from the $J = \frac{5}{2}$ crystal field split states of the $Ce^{3+}$ ion. The position of the higher temperature peak ($\sim 160$ K) is associated with the crystal field splitting between the multiplets of the lowest spin–orbit split $J = \frac{3}{2}$ level of the $Ce^{3+}$ ions. The 160 K peak is
Fig. 10.38. The calculated energy dependence of the $f$ electron density of states $\rho_f(E, T)$ for the single-impurity Anderson model, at various temperatures. The calculation is appropriate to describe a Ce ion in a cubic environment. The temperature dependent Kondo peak, above the Fermi energy, is split by the crystalline electric field. The spectrum was calculated using the non-crossing approximation produced by the freezing out of transitions into the higher crystal field split states [165, 228]. For temperatures greater than the crystal field splitting, the conduction electrons participate in scattering events in which the Ce$^{3+}$ ions are scattered between all the crystal field split states of the $J = \frac{5}{2}$. However, for temperatures below the crystal field splitting of the lowest multiplet, only the lowest crystal field multiplet contributes to the scattering rate. Hence, as the coefficient of the $\ln T$ term in the resistivity is determined by the effective degeneracy of the local moments, the drop in effective degeneracy produces the second peak in $\rho(T)$ for CeCu$_2$Si$_2$. In contrast to Ce systems [229–233], $U$ based heavy-fermion systems show little evidence of crystal field splittings or, if they do, are ambiguous [235–237]. For single impurity spin–flip scattering, the logarithmic temperature variation of the resistivity is expected to cease near $T_K$, below which the resistivity should show a Fermi liquid like $\rho(T) = \rho(0) - A T^2$ temperature variation with a resistivity maximum only occurring at zero temperature. In contrast to theoretical results for the single-impurity Kondo model, for heavy-fermion materials such as CeAl$_3$, CeCu$_2$Si$_2$, CeCu$_6$, URu$_2$Si$_2$ and UBe$_{13}$, the observed Kondoesque increase in the resistivity is followed by a rapid decrease with decreasing temperature. The decrease is often attributed to the onset of coherence in the set of $f$ moments. Above the coherence temperature, the $f$ moments are as-
Fig. 10.39. The temperature dependence of the electrical resistivity of CeCu$_2$Si$_2$, plotted on a logarithmic temperature scale. The two regions where the resistivity shows an approximate $lnT$ dependence are indicated by the solid lines. [After Franz et al. (1979), [227]]

assumed to be independent and have uncorrelated fluctuations whereas at low temperatures, the moments are assumed to approximately align over large spatial regions. The fluctuations responsible for preventing perfect alignment are assumed to have a collective character, and it is these fluctuations that are assumed to provide the dominant inelastic scattering process that freezes out as $T$ is reduced to zero. In URu$_2$Si$_2$, the broad peak in the resistivity occurs at 50 K where it attains a value of 3000 $\mu$Ωcms and then shows a rapid decrease at lower temperatures. The decrease is briefly interrupted at $T_N = 17.5$ K, where the resistivity shows a slight, but abrupt, increase due to ordering [21]. The increase in the resistivity is understood in terms of a partial gapping of the Fermi surface and is consistent with the change in the extrapolated $C/T$ ratio from 112 mJ/mole K$^2$ above $T_N$ to 65.5 mJ/mole K$^2$ below $T_N$. In UBe$_{13}$, the peak in the resistivity is remarkably sharp; the peak occurs at 2.5 K and has a value of the order of 200 $\mu$Ωcm. On the other hand, UPt$_3$ and UAl$_2$ do not show Kondo-esque maxima in the resistivities but just decrease with decreasing temperature. The low temperature resistivities of CeCu$_6$, CeAl$_3$, UAl$_2$, UPt$_3$, UGe$_2$ under pressure and Yb-BiPt show $\rho(T) = \rho(0) + A T^2$ temperature variations characteristic of electron–electron scattering. The coefficients of the $T^2$ terms are enormous as they seem to scale with the square of the $\gamma$ term in the specific heat [238], in agreement with the argument involving highly enhanced quasi–particles. The large $A$ coefficients are, therefore, taken as indicating the mutual scattering of quasi–particles in a highly enhanced Fermi liquid. Although a large $T^2$ coeff-
ficient was also observed in the resistivity of CeCu$_2$Si$_2$, it has been suggested that this is not a true manifestation of the existence of a Fermi liquid in that by suppressing the superconductivity through the application of a magnetic field, a $T^{3/2}$ temperature variation is observed in $S$ type samples [192]. Since the specific heat of $S$ type samples also shows non–Fermi–liquid like behavior, it has been suggested that the non–Fermi–liquid is caused by the existence of a quantum critical point, but could also be due to structural disorder [193].

The residual resistivities $\rho(0)$ of heavy–fermion materials are sensitive to the presence of disorder and impurities. Often the residual resistivity is found to have a magnitude comparable to that of common metals with similar levels of impurities. However, in cases where the $f$ ion is substituted by a non–magnetic impurity, the resulting residual resistivities are quite large. This has led to the concept of the Kondo hole in which a substitutional non–magnetic impurity at an $f$ site of a heavy–fermion system produces a scattering phase shift of $\frac{\pi}{2}$ relative to the coherent resonant scattering of the lattice of $f$ ions. Since the difference of the phase shifts is close to $\frac{\pi}{2}$, the scattering of the substitutional non–magnetic impurity is similar to the scattering produced by a magnetic impurity in a simple metal [239]. Basically, the large residual resistance of a Kondo hole in a heavy–fermion metal can be attributed as being due to the persistence of the large mass renormalization of the current carrying quasi–particle in the presence of disorder. This is to be expected as current can only be carried by states that are spatially extended. On the other hand, the scattering time at the site of the non–magnetic impurity is not expected to be renormalized by the mass enhancement factor as the scattering is purely a local phenomenon taking place on the non–magnetic impurity ion. The identification of the wave function renormalization $Z$ with the ratio $\Delta/k_B T_K$ then yields a residual resistivity that is governed by the characteristic Kondo scattering rate of the missing $f$ ion.

**Magneto–Resistance**

Since large amplitude fluctuations of the magnetic moments are assumed to be responsible for the transport scattering rate, the field dependence of the resistivity or longitudinal magneto–resistance should be quite illuminating. Basically, the application of a sufficiently large magnetic field could result in a partial ordering of the moments thereby suppressing the magnetic fluctuations and producing a reduction of the resistivity. This expectation is borne out in experiments on CeCu$_6$ [240] and in the normal state of UBe$_{13}$ [241,242] which show large negative magneto–resistances, $\Delta \rho(H)$,

$$\frac{\Delta \rho(H)}{\rho(0)} = \frac{\rho(H) - \rho(0)}{\rho(0)}.$$  \hspace{1cm} (10.143)

On the other hand, for both CeAl$_3$ [243,244] and CeCu$_2$Si$_2$ [243], the magneto–resistance is negative at sufficiently high temperatures and changes sign at temperatures comparable to the cross–over temperature. The high temperature magneto–resistance shows a scaling with field which can be understood.
in terms of models of magnetic scattering from single impurities [245, 246] in which Zeeman splitting suppresses the incoherent resonant scattering. However, the single impurity models fail at low temperatures where the incoherent magnetic scattering ceases [241, 247]. In this low temperature limit, one expects that the resistivity will be dominated by impurity scattering and that the magneto–resistivity should follow the scaling implied by Koehler’s law. In UBe$_{13}$, the low temperature magneto–resistance is very large, negative, and anisotropic, which is indicative that the magnetic fluctuations responsible for the scattering of the conduction electrons are also anisotropic [248]. For UPt$_3$ and UAl$_2$, which have no maxima in the resistivity, the magneto–resistances are positive [249]. A positive transverse magneto–resistance is often found in common metals with multi–sheeted Fermi surfaces. In these common metals, the Lorentz force produces different shifts of the various sheets of Fermi surface that only produce a zero transverse current when their contributions are combined. The Lorentz force acting on the transverse current components produces a positive magneto–resistance. Therefore, the positive magneto–resistances found at low temperatures can be regarded as providing signatures that the quasi–particles are itinerant.

**The Hall Effect**

The application of a static magnetic field perpendicular to the direction current flow in a metal, produces a voltage drop in a direction that opposes the Lorentz force acting on the moving electrons. The Hall coefficient, $R_H$, describes the dependence of the ratio of the transverse electric field to the current on the strength of the applied field. In conventional metals, the Hall coefficient is almost temperature independent and provides information about the density and the sign of the charge carriers. However, in heavy–fermion systems, the Hall coefficient is about two orders of magnitude larger than in conventional metals and is also highly temperature dependent. At room temperature, the Hall coefficient is usually positive and initially increases with decreasing temperature and then goes through a maximum. The maximum has been observed in CeCu$_6$ [250], CeCu$_2$Si$_2$ [251], UBe$_{13}$ [252] and UPt$_3$ [253]. The temperature dependence of the Hall coefficient of UPt$_3$ is shown in Fig. 10.40. For systems for which the resistivity has a maximum, the temperatures of the maximum in the Hall coefficients and the temperatures of the corresponding resistivity maxima are comparable [250]. The high temperature variation of the Hall coefficient is interpreted in terms of the combination of the usual Hall effect due to the Lorentz force and also from skew scattering. The skew scattering results from the scattering of conduction electrons from a set of independent magnetic impurities. The skew scattering involves the polarization of the moments by the applied magnetic field which also produces a spin–splitting in the impurity $f$ density of states. The spin–orbit coupling on the impurity results in interference between the $l = 3$ and $l = 2$ angular momentum channels [254]. The extreme sensitivity of the narrow quasi–particle density of states at the Fermi energy has been
Fig. 10.40. The temperature dependence of the Hall coefficient of UPt$_3$ measured in a 4-T field. [After Schoenes and Franse (1986), [253].] The solid line is a fit to an expression for incoherent skew scattering identified [255] as the source of the very large magnitude of the Hall coefficient. The anomalous skew scattering from independent local moments does reproduce the high temperature behavior of the Hall coefficient but fails to predict the maximum in the Hall coefficient, which is followed by a rapid drop at lower temperatures. The drop in the Hall coefficient has been interpreted as signifying the onset of coherence between the fluctuating parts of the local magnetic moments. In some heavy-fermion materials such as UAl$_2$, the Hall coefficient changes sign at low temperatures. Similar sign changes in $R_H$ can be found in materials that have multi-sheeted Fermi surfaces.

**Thermopower**

It is expected that the low temperature limit of the thermopower $S$ should be un-renormalized by the quasi-particle mass enhancement. Nevertheless, the measurement is expected to reflect the strong interactions as it should provide a measure of the logarithmic derivative of the imaginary part of the self-energy. This can be seen from the usual expression of the linear $T$ contribution in terms of the ratio of two correlation functions

$$ S = -\beta \frac{K_{11}}{K_{12}} , $$

(10.144)
where $K^{11}$ involves the time ordered current–current correlation function, and $K^{12}$ involves the heat flux–current correlation function

$$K^{11} = \frac{1}{3} \int_0^\beta d\tau \exp\left[i \omega \tau\right] < T, j(\tau) \cdot j(0) >,$$

$$K^{12} = \frac{1}{3} \int_0^\beta d\tau \exp\left[i \omega \tau\right] < T, j_Q(\tau) \cdot j(0) >,$$

(10.145)

where $j$ is the current density and $j_Q$ is the heat flux. The Seebeck coefficient can be approximately evaluated as

$$S = -\frac{1}{e |T|} \frac{I^{(1)}}{I^{(0)}}.$$  

(10.146)

When the above expression is analyzed using the Sommerfeld expansion, one finds the relation

$$S = \frac{\pi^2}{3} k_B^2 T \left| \frac{\partial \text{Im} \Sigma(E)}{\partial E} \right|_{E=0} \frac{\text{Im} \Sigma(E)}{\text{Im} \Sigma(E)}$$

(10.147)

which also shows that $S$ should vanish linearly with $T$ at low temperatures. The measured thermopowers show considerable variation both with compound and with temperature but do share one common characteristic, which is that the magnitude of $S$ is about an order of magnitude larger than common metals. At 4 K, the thermopower of UBe$_{13}$ is $-11 \mu$VK$^{-1}$ [256] and has decreased to $-25 \mu$VK$^{-1}$ just below 1 K where the superconductivity sets in. At high temperatures, the thermopowers of CeCu$_2$Si$_2$ [2] and UAl$_2$ [257] are both positive, and have magnitudes of 15 $\mu$VK$^{-1}$ and 40 $\mu$VK$^{-1}$, respectively, while in the same temperature range $S$ for UPt$_3$ is negative with a magnitude of about $-12 \mu$VK$^{-1}$. The compound CeCu$_2$Si$_2$ has a shallow maximum in $S$ of about 20 $\mu$VK$^{-1}$ at 170 K, which seems to be connected with the crystal field splitting observed in this compound, while the thermopower of UPt$_3$ appears to have an even shallower minimum of $-12 \mu$VK$^{-1}$ near 200 K. The thermopower of UPd$_2$Al$_3$ is large and shows a monotonic decrease with decreasing temperature [258]. These slow variations of $S$ in the high temperature region, are to be contrasted with the variations [259] found in CeCu$_6$ and CeAl$_3$, where $S$ decreases from about 40 to 10 $\mu$VK$^{-1}$ as $T$ is increased from 50 and 300 K. The thermopower of UPt$_3$ changes sign at 24 K, and has a positive peak at about 8 K. The thermopower in CeCu$_2$Si$_2$ changes sign at 75 K from positive to negative with decreasing temperature, and there is a deep minimum ($-35 \mu$VK$^{-1}$) at 20 K near the cross-over temperature. This is followed by a small positive maxima at a temperature of 0.2 K. The thermopower of CeAl$_3$ [260] is similar to CeCu$_2$Si$_2$ in that it goes through a minimum ($-4 \mu$VK$^{-1}$ at 3.5 K), changes sign near the crossover temperature, and shows a small positive maximum at an even lower temperature ($\sim 0.3$ K). However, CeCu$_6$ has three positive maxima [259], while
UAl\textsubscript{2} only shows one negative minimum before tending to zero linearly with $T$ \cite{257}. This rich variety of behavior is not reconcilable with the behavior of a single impurity Kondo model in which the scattering is dominated by the position of the Kondo resonance with respect to the Fermi–level. For Ce impurities, the model predicts that $S$ has a positive maximum at the Kondo or cross–over temperature and falls to zero as $T \to 0$. The richness of the low temperature variations of the thermo electric power, like the Hall effect and the de Haas van Alphen measurements, suggests that the electronic structure contains a number of quasi–particle bands with high effective masses near the Fermi energy.

**Thermal Conductivity**

The thermal conductivity of metals, unlike the electrical conductivity, has contributions from the non–equilibrium distribution of phonons as well as from the quasi–particles. Thus, one may write

$$\kappa = \kappa_L + \kappa_c$$ \hfill \text{(10.148)}

where $\kappa_L$ represents the lattice contribution and $\kappa_c$ is the electronic contribution. There is no simple experimental way to decouple these two terms without recourse to theory. It is expected that, at sufficiently low temperatures, one will have

$$\kappa_L \propto T^2,$$ \hfill \text{(10.149)}

when the phonon scattering is due to electron–phonon interactions, and if the mean free path is less than the size of the crystal. Otherwise, one expects

$$\kappa_L \propto T^3$$ \hfill \text{(10.150)}

when the phonons mainly scatter from the surfaces of the crystal. At temperatures much greater than the Debye temperature, $T \gg \Theta_D$, one expects that the lattice contribution to the thermal conductivity will have the temperature dependence

$$\kappa_L \propto \frac{1}{T}.$$ \hfill \text{(10.151)}

These considerations lead one to conclude that, at sufficiently low temperatures, the quasi–particle contribution is the dominant term in the thermal conductivity. The quasi–particle contribution to the thermal conductivity is usually written as

$$\kappa_c = \frac{\pi^2}{9} k_B T \left( v^2 \tau \rho_{qp}(E) \right) \bigg|_{E=0},$$ \hfill \text{(10.152)}

where $\tau$ is the scattering rate, and $v$ is the quasi–particle velocity ($\tau \sim Z \tau_0$ and $v \sim \frac{\hbar}{\tau m_0}$). The two factors of the mass renormalization $Z$, occurring in
the quasi–particle velocities, are expected to cancel with a similar factor in
the quasi–particle density of states and also with one factor of \( Z \) in the quasi–
particle lifetime. Hence, the overall magnitude of the electronic contribution
of the low temperature thermal conductivity should not differ significantly
from that of a normal metal, for reasons similar to why the d.c. electrical con-
ductivity is also unrenormalized. Thus, one expects that the Lorentz number,
\( L(T) \), defined by

\[
L(T) = \frac{\kappa_e(T)}{T \sigma(T)}
\]

(10.153)

should have a value similar to the value \( L_0 \) predicted for purely elastic scattering

\[
L_0 = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2.
\]

(10.154)

For purely elastic scattering, the Lorentz number, involving the ratio of the
appropriate conductivity tensors, is expected to be isotropic. Since inelastic scattering results in a reduction of the quasi–particles’ energies, in addition to
the reduction in the quasi–particle current, the Lorentz number is expected
to be reduced below \( L_0 \) when inelastic scattering is also present. Since stoi-
chiometric heavy–fermion materials often show sizeable \( T^2 \) terms in the low
temperature electrical resistivity which are attributed to (inelastic) electron–
electron scattering, one expects that when the \( T^2 \) term is larger than the
residual resistivity, \( L(T) \) should have a value close to that for purely elastic
Baber scattering [261]

\[
L_{clas} = L_0 \left( \frac{36}{\pi^2} - 3 \right).
\]

(10.155)

However, for lower temperatures such that the quasi–particle–quasi–particle
scattering term becomes negligible compared with the residual resistivity, one
should recover higher values of \( L(T) \) close to the Lorentz number \( L_0 \). These
expectation are very nearly borne out by experiments on the normal states
of CeAl$_3$, CeCu$_6$, CeCu$_2$Si$_2$ and UPt$_3$. In CeAl$_3$ [260, 262, 263], the Lorentz number exhibits a minimum value of 0.75 \( L_0 \) at 0.5 K, which is larger than
the theoretical limit of 0.65 \( L_0 \), and it overshoots the elastic limit yielding a
weak maximum at 1.1 \( L_0 \) at 50 mK. The temperature of the minimum roughly
agrees with the temperature where the \( T^2 \) term dominates the resistivity. For
CeCu$_6$, the Lorentz number falls to a minimum value smaller than \( L_0 \) at a
temperature of about 0.3 K, which is close to the temperature of 0.15 K where
the \( T^2 \) term in the resistivity first becomes apparent as it cools [264]. The
extrapolated data show that \( L(T) \) approaches \( L_0 \) at 20 mK, in agreement
with the arguments concerning the freezing out of the inelastic scattering
processes. For CeCu$_2$Si$_2$, the low \( T \) value of \( L(T) \) appears to be \( L_0 \) [2,265]. At
low temperatures, the inferred phonon contribution to $\kappa_L$ of CeCu$_2$Si$_2$ has a $T^2$ variation [265] as expected from electron–phonon scattering. The phonon contribution $\kappa_L$ starts to become larger than the electronic component at the temperature of 1 K where on cooling the $T^2$ term in the resistivity first becomes apparent [265]. For UPt$_3$, the minimum value of 0.45 occurs at a temperature of the order of 2 K [266, 267]. Since UBe$_{13}$ does not form a Fermi liquid, it is not surprising that the Lorentz number is not constant but instead varies approximately linearly with temperature [28, 268].

For temperatures greater than the coherence temperature, the Fermi liquid analysis of $\kappa_e$ is expected to fail. However, in the temperature regime where $T > T_K$, one expects that Ce based heavy–fermion materials will resemble a metal in which the conduction electrons scatter off of a set of independent disordered magnetic moments. In this temperature regime, the thermal conductivity from the electrons may be calculated perturbatively [269]. The result for the Lorentz number $L(T)$ can be approximately expressed in the form

$$L(T) = \frac{1}{e^2 T} \left( \frac{I^{(2)}}{I^{(0)}} - \left( \frac{I^{(1)}}{I^{(0)}} \right)^2 \right),$$

(10.156)

where $I^{(n)}$ is defined by Eqn. (10.141). The Lorentz number is also expected to depend strongly on the crystal field splittings [270]. The crystal field splitting in CeCu$_2$Si$_2$ is assumed to give rise to a minimum in the Lorentz number at the temperature around 80 K. In this high temperature regime, the Lorentz number can be appreciably greater than $L_0$. This result is caused by the large temperature induced shift of the $f$ density of states away from the Fermi energy for $T > T_K$. The experiments are consistent with this trend: However, the lattice contribution to $\kappa_L$ is no longer negligible and may be several times greater than the quasi–particle contribution. This hypothesis is supported by the comparison of measurements on CeCu$_2$Si$_2$ with the reference material LaCu$_2$Si$_2$. In fact, if the phonon contribution $\kappa_L$ is completely ignored in the data analysis, the Lorentz number is about a factor of twenty times greater than $L_0$. The inferred presence of a large phonon contribution is also supported by the conclusion that the theoretical calculated values of $L(T)$, using the independent Kondo impurity model, are unable to account for electronic contributions to $L(T)$ of this magnitude. Likewise, for UPt$_3$, the phonon contribution has been identified as being important above 3.5 K [29] and may be responsible for up to a maximum of 4.5 $L_0$ of the Lorentz number at $T = 24$ K inferred from the raw data [267]. The Lorentz number for CeCu$_6$, in the high temperature regime [271] qualitatively resembles $L(T)$ for UPt$_3$, having a maximum at $T \sim 20$ K where it attains a value of about 2.5 $L_0$ but falls towards $L_0$ at higher temperatures.

**Ultrasonic Attenuation**

Ultrasonic experiments measure the attenuation and velocities of sound waves and, through the electron–phonon interaction, provide information about the
At temperatures much lower than the Debye temperature, the attenuation of the sound wave due to anharmonic phonon interactions should be negligible, and the electron–phonon interaction should provide the dominant contribution to the attenuation. In this case, one expects a strong similarity between the ultrasonic attenuation coefficient and the electrical conductivity. Just like the optical conductivity $\sigma(\omega)$ yields the lifetime of a photon, the ultrasonic attenuation $\alpha_{q,\omega}(\omega)$ yields the lifetime of a phonon. This similarity is expected since, for many purposes, the effect of a phonon can be interpreted in terms of the effect of the accompanying electric field. In analogy with the conductivity, one expects that in the limit $q \to 0$, the renormalization of the scattering rate will cancel with the mass enhancement. Thus, in the long wavelength limit, the ultrasonic attenuation is expected to be unrenormalized. The most noticeable difference between ultrasonic attenuation and optical absorption occurs through the extremely different magnitudes of the velocities of the corresponding waves. If the conditions allow the heavy quasi–particles to co–move with the sound wave, it becomes possible for the quasi–particles to surf–ride and continuously absorb energy from the sound wave. For example, if a longitudinally polarized sound wave with phase velocity $\frac{\omega}{q}$ propagates through a gas of heavy quasi–particles, it strongly perturbs the quasi–particles with velocities almost parallel and almost equal to the phase velocity of the wave. In the frame of reference travelling with the wave, the quasi–particle is at rest and experiences an essentially time independent electric field. The electric field continuously transfers energy from the wave to the quasi–particles that have the same velocity. If there is a slight mismatch in the velocities, quasi–particles with lower velocities than the wave draw energy from the wave and accelerate, whereas quasi–particles that are moving faster lose energy and slow down. This results in the rate of energy loss of the wave being proportional to the derivative of the distribution of quasi–particle velocities, which is evaluated at the velocity of sound. At temperatures below those at which the heavy quasi–particles are being formed, the Fermi velocity is comparable to the sound velocity in contrast to normal metals. So the attenuation of sound waves may be expected to be larger than in ordinary metals. On the other hand, due to the approximate equality between the sound velocities [272], the Born–Oppenheimer approximation no longer applies and the sound wave may have to adjust adiabatically to the quasi–particles’ motions. The induced coupling of the phonon modes can also lead to damping. It is found that the ultrasonic attenuation for CeCu$_6$, UPt$_3$, and UBe$_{13}$ have magnitudes comparable to that of ordinary metals [27]. This suggests that the magnitude of the coupling between the quasi–particle and sound wave is reduced from that observed in normal metals due to the appearance of vertex corrections. Nevertheless, the strong electron–phonon coupling shows up in other elastic properties. In ordinary metals, the attenuation is relatively featureless and is described by
a Drude–like formula,

\[ \alpha(\omega) = \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \frac{\lambda^2 \rho(\mu)}{\rho \ c^3}, \]  

(10.157)

where \( \lambda \) is the electron–phonon coupling, \( c \) is the velocity of sound, and \( \rho \) is the mass density. In heavy–fermion compounds at high temperatures, the magnitude and frequency dependence of the attenuation is reasonably similar to normal metals. However, anomalous temperature dependences are observed in the low temperature quasi–particle phases. The temperature dependence of the attenuation of longitudinal sound in UPt\(_3\) shows an anomalous peak at 12 K [273], and has an amplitude that scales with the square of the frequency of sound. The temperature dependence of the attenuation coefficient is shown in Fig. 10.41. Since the anomaly is only present in the absorption of longitudinal sound but not of transverse sound, the origin of this peak has been ascribed by Schotte et al. [274] to the existence of a breathing mode. In the breathing mode, the lattice adjusts locally to the state of the f ion, and vice versa. Thus, the sound waves are coupled to the heavy quasi–particle bands. This type of coupling is also expected to modify the phonon dispersion relations due to hybridization with the quasi–particle bands. At temperatures above 12 K, the heavy quasi–particle masses have not fully formed, and so the coupling becomes incoherent. Thus, the effect of an increase in temperature results in a reduction of the attenuation coefficient. Since in the model of Schotte et al. the sound wave mainly couples to the
thermally excited quasi–particles, the coupling is ineffective in attenuating sound at temperatures lower than 12 K. Therefore, the sound wave attenuation diminishes for temperatures lower than the peak temperature. At still lower temperatures, but still in the normal state, the attenuation coefficient of \( \text{UPt}_3 \) decreases proportional to \( T^2 \) with increasing temperatures [30]. This is indicative of the \( T^2 \) dependence of the quasi–particle scattering rate. The observation of an anomalous peak in the phonon density of states [275] provides supporting evidence for the validity of the breathing mode picture of \( \text{UPt}_3 \). The attenuation of longitudinal sound waves in \( \text{CeCu}_6 \) [276] is somewhat similar to that of \( \text{UPt}_3 \) in that it shows a peak below a temperature of 10 K. However, unlike \( \text{UPt}_3 \), the intensity of the peak in \( \text{CeCu}_6 \) scales linearly with frequency. Furthermore, the peak broadens and shifts to higher temperatures with increasing phonon frequency.

10.3.3 Dynamic Magnetic Properties

Just as the effects of the collective magnetic fluctuations and the low temperature gas of heavy quasi–particles show up in the transport and thermodynamic properties of heavy–fermion materials, the effects of these excitations also show up in the magnetic properties.

Nuclear Magnetic Relaxation

In the presence of an applied static magnetic field, a nuclear spin relaxes to its ground state through interaction with the fluctuations of the electronic magnetic moments. On assuming that the coupling is weak so that the Born Approximation is valid, the longitudinal relaxation rate \( 1/T_1 \) can be expressed in terms of the hyperfine field coupling \( A_{hf}(\vec{r} - \vec{r}') \) between the nuclear spin point \( \vec{r}' \) to the magnetization density \( \vec{M}(\vec{r}) \) and the dynamic susceptibility \( \chi^{+,-}(q; \omega) \) via

\[
\hbar T_1^{-1} = k_B T \frac{1}{N} \sum_{q} \left| A_{hf}(q) \right|^2 \left[ \frac{\text{Im} \chi^{+,-}(q; \omega_N)}{\hbar \omega_N} \right]. \tag{10.158}
\]

In this, \( A_{hf}(q) \) is the spatial Fourier transform of the hyperfine field, and \( \omega_N \) is the nuclear Larmor frequency which, in conventional metals, can be neglected as it is much smaller than the lowest energy scale for the electrons. The dynamic magnetic susceptibility is the spatial and temporal Fourier transform of the quantity \( \chi^{\alpha,\beta}(r; t) \) defined by the causal correlation function involving the commutator of the components of the magnetization density

\[
\chi^{\alpha,\beta}(r; t) = -\frac{i}{\hbar} \langle \left[ M^\alpha(r; t), M^\beta(0; 0) \right] \rangle \Theta(t), \tag{10.159}
\]

where \( \Theta(t) \) is the Heaviside step function. In the paramagnetic state, the susceptibility tensor is spin rotationally invariant so one has

\[
\chi^{x,x}(r; t) = \chi^{y,y}(r; t) = \chi^{z,z}(r; t) = \frac{1}{2} \chi^{+,-}(r; t). \tag{10.160}
\]
Due to the Shiba relation \[277\], one expects that, for a local paramagnetic Fermi liquid in the limit \( \omega \to 0 \), the imaginary part of the susceptibility should satisfy the equation

\[
\lim_{\omega \to 0} \left( \frac{2J+1}{3} \right) \frac{\text{Im} \chi^{z,z}(0; \omega)}{\hbar \omega} = \pi \left( \frac{\chi^{z,z}(0; 0)}{g \mu_B} \right)^2.
\] (10.161)

This suggests that, with a \( q \) independent hyperfine coupling, the longitudinal nuclear relaxation rate of heavy–fermion systems should vary as the square of the low temperature static susceptibility or the square of the \( \gamma \) coefficient in the specific heat, much the same as the correlation between the coefficient of the \( T^2 \) term of the resistivity and the linear \( T \) term in the specific heat found by Kadowaki and Woods \[238\]. For materials such as UBe\(_{13} \) \[278\], the scaling with the square of the quasi–particle density of states is not followed due to the \( q \) dependence of the coupling and vertex corrections. Nevertheless, magnetic relaxation experiments on heavy–fermion compounds at low temperatures do show the linear \( T \) Korringa relaxation rate with an enhanced magnitude, indicating the existence of heavy quasi–particles.

The Knight shift \( K \) is a shift in the nuclear resonance field which provides a measure of the induced field at the site of the nucleus due to the polarization of the electronic system. It is often found that the induced field is dominated by the bulk static susceptibility \( \chi^{z,z}(0; 0) \) of the \( f \) electrons and so can be used as an estimate of the strength of the average hyperfine field

\[
K = \frac{A_{hf}}{g_N \mu_N} \chi^{z,z}(0; 0).
\] (10.162)

Assuming a local isotropic hyperfine field and isotropic \( q \) independent magnetic fluctuations, one finds the dimensionless Korringa product

\[
S = k_B T K^2 \frac{T_1}{\hbar}
\] (10.163)

has the theoretical value

\[
S_0 = \frac{(2J+1)J(J+1)}{6 \pi} \left( \frac{g_e \mu_B}{g_N \mu_N} \right)^2
\] (10.164)

for ions with magnetic moment \( J \). Corrections must be made to this relation for heavy–fermions compounds with anisotropic susceptibilities. The magnitude of the Korringa ratio is defined as \( S S_0 \). Since the relaxation rate involves a sum over all \( q \), deviations from the ideal value of the Korringa ratio may be used to infer the relative magnitude of the \( q \) averaged susceptibility to the uniform \(( q = 0 )\) susceptibility.

The Knight shift and the longitudinal relaxation rate can be used to estimate the typical frequency of local moment fluctuations. Assuming a phenomenological \( q \) independent relaxational form for the dynamic susceptibility

\[
\chi^{z,z}(\omega) = \chi^{z,z}(0) \frac{\Gamma}{\Gamma - i \hbar \omega},
\] (10.165)
where $\Gamma$ is the relaxation rate, one finds that, if $h \omega_N \ll \Gamma$, the transverse relaxation rate can be expressed in terms of the limit

$$\lim_{\omega_N \to 0} \frac{Im \chi_{z,z}(\omega_N)}{h \omega_N} = \frac{\chi_{z,z}(0)}{\Gamma}.$$ \hspace{1cm} (10.166)

Thus, the spin–fluctuation energy is estimated as

$$\Gamma = 2 k_B T \frac{T_1}{h} | A_{hf} |^2 \chi_{z,z}(0) \hspace{1cm} (10.167)$$

Above the Néel temperature, the NMR longitudinal relaxation rate of UPt$_3$ is linear in $T$ [31], but below $T_N$, has a large anisotropic coefficient that varies from 1810 to 1050 sec$^{-1}$ K$^{-1}$ for fields parallel and perpendicular to the crystalline c–axis [279]. The anisotropy of the relaxation rate (shown in Fig. 10.42) is accompanied by a large anisotropic Knight shift [280] which reflects the anisotropy of the bulk susceptibility. From estimates of the hyperfine field taken from the Knight shift, a $q$ averaged fluctuation energy $\Gamma$ of the order of 9 meV was deduced from the measurements. This energy is quite large when compared with the temperature scale over which the large specific heat $\gamma$ value develops. The Korringa ratio was found to be of the order of 1.2, which indicates that the system supports low–energy paramagnon excitations, consistent with the finding of a $T^3 \ln T$ term in the low temperature specific heat.

The linear $T$ dependence of the longitudinal relaxation rate in UBe$_{13}$ has been observed for temperatures less than $T = 1.5$ K, which is much lower
than the temperature of 10 K, where the specific heat enhancement starts forming. The Korringa ratio is only 0.3, which is much reduced from the ideal value, suggesting the presence of strong antiferromagnetic correlations [281].

Below the temperature of about $T = 70$ K, the longitudinal relaxation rate of URu$_2$Si$_2$ follows the Korringa linear $T$ dependence indicative of the formation of a Fermi liquid. This linear dependence is interrupted at the Néel temperature of $T_N = 17.5$ K, and the relaxation rate again follows a linear law a little below $T_N$, but with a reduced coefficient [282, 283]. The temperature dependence of $1/T_1$ for URu$_2$Si$_2$ is shown in Fig. 10.43. The data does not show any sign of a spin–wave contribution to the relaxation process. For non–interacting quasi–particles, the coefficient of the $T$ term in the Korringa rate is proportional to the square of the quasi–particle density of states. Thus, the drop in the coefficient of $T$ found on entering the Néel state is indicative of a partial gapping of the Fermi surface. This is consistent with the drop in the specific heat $\gamma$ from 180 mJ mol$^{-1}$ K$^{-2}$ above to 50 mJ mol$^{-1}$ K$^{-2}$ below the transition. Although no direct evidence of antiferromagnetic ordering was observed in NMR measurements at ambient pressure, experiments
Fig. 10.44. The temperature dependence of the spin–lattice relaxation rate $1/T_1$ for $^{27}$Al in UNi$_2$Al$_3$. [After Kyogaku et al. (1993), [284]]

at $P = 8.3$ k bar [225] show a well defined splitting of the resonance line at $T_N$. The splitting is consistent with the staggered exchange splitting from a type I antiferromagnetic structure. In addition, the NMR spectra showed a substantial contribution from the un–split resonance line that continued, but diminished in intensity as the temperature was reduced below the Néel temperature. Since the magnitude of the staggered exchange field starts levelling off below 15 K, and as the ratio of intensities of the split and un–split lines continuously change with $T$, it has been suggested that regions of antiferromagnetism and paramagnetism coexist inside the single crystal sample but with temperature dependent volume fractions. The interpretation based on the temperature and pressure dependent volume fractions of the two phases is consistent with the spontaneous magnetic moments inferred from neutron diffraction experiments under pressure [226]. However, as the magnitude of the specific heat jump at $T_N$ does not scale with the volume fraction, it has been suggested that another (as yet unknown) type of ordering also occurs at $T_N$.

The temperature dependence of $1/T_1$ of UPd$_2$Al$_3$ [284] is very similar to that found in URu$_2$Si$_2$, in that it shows a Korringa rate that shows a partial reduction of the density of states at the Fermi energy on entering the magnetically ordered state. The properties of UNi$_2$Al$_3$ are quite different from UPd$_2$Al$_3$, in that the Korringa law does not apply above $T_N = 4.2$ K, and any linear $T$ coefficient is quite small. As seen in Fig. 10.44, the magnetic transition is marked by a peak in $1/T_1$, which is indicative of strongly antiferromagnetically coupled local moments. At lower temperatures, superconductivity occurs before any linear $T$ region develops. When a sufficiently
large magnetic field is applied to suppress the superconductivity, a linear $T$ dependence can be resolved.

The longitudinal magnetic relaxation rates have been measured at the Cu site of CeCu$_6$ [285] and at the Cu and Si sites of CeCu$_2$Si$_2$ [278, 286, 287]. In CeCu$_2$Si$_2$, the low temperature relaxation rate varies linearly with $T$ up to $T = 5$ K, but has a coefficient of proportionality of 5 sec$^{-1}$ K$^{-1}$. This large value of the slope should be contrasted with the corresponding slope of 0.025 sec$^{-1}$ K$^{-1}$ found in the compound LaCu$_2$Si$_2$, which does not contain any $f$ electrons. The enhanced value of the low temperature relaxation rate is even more apparent in CeCu$_6$, where $1/T_1$ follows a linear Korringa law below about $T = 0.2$ K with a slope of 88 sec$^{-1}$ K$^{-1}$ [285]. The relaxation rates for CeCu$_6$ and CeRu$_2$Si$_2$ are shown in Fig. 10.45. At higher temperatures, the relaxation rate of CeCu$_6$ starts changing form and shows a plateau associated with the cross-over temperature $T_K$ of 12 K, and above this, it shows a slow decrease with increasing temperature due to the Curie–like variation of the susceptibility. From the temperature variation of the longitudinal relaxation rate, one finds that the low temperature Fermi liquid in CeCu$_6$ only starts forming at a temperature lower than the cross-over temperature by a factor of 60, whereas for UBe$_{13}$ this ratio is estimated to be about 9. It is noteworthy that the result for CeCu$_6$ does not show the scaling expected from the single-impurity Anderson model, despite the fact that the non-local contributions to the magnetic response found from neutron scattering are estimated as being only 10% . However, the ratio found for UBe$_{13}$ is more in line with the expectation based on the single-impurity Anderson model [288] despite the presence of strong antiferromagnetic correlations as indicated by the Korringa ratio.
The transverse magnetic relaxation rate $1/T_2$ provides information about processes whereby the nuclear spin precession is dephased and does not involve transitions where there is a change of Zeeman energy. On neglecting the effects of static random local fields, the transverse relaxation rate is given by perturbation theory as

$$
\left( \frac{\hbar}{T_2} \right)^2 = \frac{3}{4} I(I + 1) |A_{hf}|^4 \left[ \frac{1}{N} \sum_{q} \chi^2(q) - \left( \frac{1}{N} \sum_{q} \chi(q) \right)^2 \right]
$$

(10.168)

which measures the non-uniform component or $q$ variation of the static susceptibility. For systems close to a magnetic instability in which $\chi(q)$ peaks up around an ordering vector $Q$, one expects that the susceptibility may have an Ornstein–Zernicke form with a correlation length $\xi$,

$$
\chi(q) = \frac{\chi(Q)}{1 + |q - Q|^2 \xi^2}.
$$

(10.169)

Thus, one finds that

$$
\left( \frac{\hbar}{T_2} \right)^2 \propto \xi^{-3} \chi^2(Q)
$$

(10.170)

and as, from the simple scaling hypothesis $\chi(Q) \propto \xi^2$, one has

$$
\frac{1}{T_2} \propto \xi^{\frac{1}{2}}.
$$

(10.171)

Thus, one expects $1/T_2$ to be enhanced in the vicinity of a magnetic phase transition. Furthermore, in the ordered state, the precession frequency is expected to be changed due to the presence of static magnetic moments or local fields. This information can be used to provide information about the size of the ordered moments.

In addition to $1/T_2$ relaxation rates, NMR linewidths are also sensitive to local static magnetic fields [289]. This has provided some additional information on the $T = 17.5$ K transition in URu$_2$Si$_2$. In this compound it was found that, for temperatures above $T_N$, the linewidth is linearly–dependent on the field and has an anisotropy similar to that of the sample’s magnetization. However, below $T_N$, the measurements also show an additional isotropic, field–independent, contribution to the linewidth which is shown in Fig. 10.46. The temperature dependence of the isotropic component is similar to that expected from a mean–field transition that occurs at $T_N$. Since at ambient pressures the signal is predominantly from the paramagnetic regions of the sample, and as (unlike the magnetic ordering) the field–independent contribution to the width is isotropic, the authors suggest that the width is due to the coupling to the unknown or “hidden” order parameter.
Fig. 10.46. The temperature dependence of the anomalous component of the $^{29}$Si line width $\lambda(T)$ in URu$_2$Si$_2$. Open circles H || to c, solid circles H ⊥ to c. [After Bernal et al. (2001), [289]]

Muon spin relaxation works in much the same way as NMR, but the zero field precession rate is much more sensitive to ordered magnetic moments with small magnitudes. Also as the muon precession frequency is extremely slow, µSR is effective in discriminating between slowly varying magnetic order and static order. Therefore, muon spin relaxation measurements have played a particularly important role in identifying magnetic phase transitions, specially as the transition to magnetically ordered phases of heavy-fermions may or may not be accompanied by specific heat anomalies. In the case of UPt$_3$, Cooke et al. [290] discovered the existence of magnetic ordering at $T_N = 5$ K through the zero field muon spin relaxation line width $1/T_2$, even though no corresponding specific heat anomaly was observed at the transition. The transverse relaxation rate showed the growth of an additional contribution below $T_N$ corresponding to an increase in the local fields due to a very small moment of order 0.01 $\mu_B$. The small magnitude of the ordered moment is presumably responsible for the absence of a specific heat anomaly at $T_N$. The existence of magnetic ordering was rapidly confirmed by neutron scattering experiments [291]. However, later muon resonance experiments on better quality samples no longer showed this feature in the muon relaxation rate [292]. This discrepancy is presumably caused by the exact cancellation of the field due to the ordered moment at the muon sites which is disrupted by the presence of disorder and thereby revealing a finite staggered magnetization.

In URu$_2$Si$_2$, the magnetic transition is accompanied by a large change in the specific heat at $T_N = 17.5$ K, but the size of the average ordered magnetic moments found from neutron and x-ray scattering are only of the
order of 0.03 $\mu_B$. Although transverse relaxation rates and Knight shift measurements do indicate that magnetic ordering occurs, the static ordered magnetic moments inferred from the muon measurements [293, 294] are an order of magnitude smaller than the average magnetic moments found from the neutron scattering experiments at ambient pressure. Due to the large magnitude of the specific heat jump and the small magnitude of the averaged ordered moments, it has been suggested [295–297] that the primary ordering is non–magnetic. However, polarized diffraction experiments and a symmetry analysis seem to rule out higher order multipolar transitions [298]. Also, measurements in applied fields do not yield evidence for exotic types of multiple spin correlations [299].

In CeAl$_3$, by contrast with URu$_2$Si$_2$ where a large specific heat anomaly is found at $T_N$, only a slight and sample dependent specific heat anomaly has been observed. However, the muon spin resonance spectrum shows evidence that magnetic order develops in CeAl$_3$ at $T = 1.5$ K [300,301]. Furthermore, near $T = 0.7$ K where the susceptibility shows a maximum, the ordered moment is quite sizeable and has been reported to be as large as 0.5 $\mu_B$ [302]. The lack of correlation between the size of the ordered moments and the size of the specific heat jump is not understood. However, the magnetic ordering does appear to show up in the resistivity of single crystals where a $T^3$ variation has been observed [303]. The $T^3$ variation is indicative of the existence of a low–energy branch of spin–wave excitations.

Evidence for static magnetic order in CeCu$_2$Si$_2$ in zero field and longitudinal field muon spin relaxation has been reported [304] just above the superconducting transition temperature $T_c = 0.7$ K. The inferred size of the ordered magnetic moments is of the order of 0.1 $\mu_B$. However, the intensity of the NQR line decreases monotonically with decreasing temperature and shows no anomalous broadening associated with ordered magnetic moments [305,306]. The magnetic ordering persists in the superconducting phase and competes with the superconductivity [307–309]. Investigations show evidence that the superconductivity and magnetic ordering may exist in separate thermodynamic phases, but these are phases for which $T_c$ and $T_N$ coincide in the best quality samples. Application of a magnetic field suppresses the superconductivity transition temperature but (initially) has no effect on $T_N$. The zero field muon spin relaxation experiments show two components that decay at rates that differ by about an order of magnitude [309]. The data can be interpreted in terms of the sample existing in two separate phases: the superconducting phase and a magnetic A phase. An estimate of the weight of these two phases can be made based on the amplitudes of the two components. For temperatures above the superconducting transition, the proportion of the A phase increases with decreasing $T$, reaching a maximum at $T_c$ with a value of $\frac{3}{4}$. The magnitude of the specific heat jump at the superconducting transition seems to scale with the relative weights of the two phases. As the temperature is lowered, the volume fraction associated with the superconduc-
tor grows by expelling the $A$ phase and saturates at about a volume fraction of $\frac{2}{3}$. The relative weights of the superconducting phase and the $A$ phase are extremely sensitive to the deviations from stoichiometry of $Ce$ [190]. Doping experiments have shown that substitutionally doping Th on the Ce sites can lead to the formation of an antiferromagnetic state with a significantly larger magnetic ordering temperature for Th concentrations of only about 7%.

**Neutron Scattering Cross-section**

The most direct way of obtaining information about the magnetic excitations in a material is through inelastic neutron scattering experiments in which momentum $h\mathbf{q}$ and energy $h\omega$ are transferred between the neutron and the sample. The neutron interacts with the electronic spins via a dipolar interaction and yields information about the imaginary part of the dynamic susceptibility. The differential scattering cross-section for an unpolarized beam of neutrons due to purely magnetic scattering, is given by

$$\frac{d^2\sigma}{d\omega d\Omega} = \frac{N}{g^2 \mu_B^2 m_e^2} \left( \frac{k}{k'} \right)^2 \left[ 1 + N(\omega) \right] |F(q)|^2 \sum_{\alpha,\beta} \text{Im}\chi_{\alpha,\beta}(q;\omega) \bigg| \delta_{\alpha,\beta} - \hat{q}_\alpha \hat{q}_\beta \bigg|.$$

(10.172)

Here, $F(q)$ is the atomic form factor for the magnetic moments, $k$ and $k'$ are the magnitude of the incident and scattered neutron wave vectors, and $N(\omega)$ is the Bose–Einstein distribution function. The above expression should also be multiplied by the Debye–Waller factor due to zero point and thermally excited lattice vibrations.

Generally, the low–energy dynamic magnetic response of a heavy–fermion system is interpreted as the sum of a large quasi–elastic relaxation contribution that is $q$ independent and $q$ dependent terms associated with spatial magnetic correlations. The relaxational component is of the form

$$\text{Im} \left[ \chi(q;\omega) \right] = A \frac{h\omega}{h^2 \omega^2 + \Gamma^2}$$

(10.173)

which is indicative of local moment fluctuations. The width of the quasi–elastic peak seems to saturate at low temperatures but increases with increasing $T$ at higher temperatures. The $q$ independence and the temperature variation of the width $\Gamma$ found in some Ce systems [230,231,310] are similar to the behaviors found in the single–impurity Anderson model [311], where

$$\Gamma(T) \sim \Gamma(0) + B \sqrt{T}.$$

(10.174)

The temperature dependence of the quasi–elastic linewidth of CePb$_3$ is shown in Fig. 10.47. The product of the zero temperature limit of the linewidth and
The linear $T$ term in specific heat, $\Gamma(0) \gamma$, should scale inversely with the Wilson ratio. For CeAl$_3$ [310], CeCu$_6$ and CeRu$_2$Si$_2$ [312,313] respectively, the product has magnitudes of 0.77, 0.67 and 0.70 J meV/mole/K$^2$, even though the widths show considerable variation with $q$. By contrast, in CePb$_3$ where no $q$ dependence was observed [314], the product is only 0.034, whereas the Wilson ratio obtained from thermodynamic measurements at the same temperatures is of the order of unity [182]. Similar narrow quasi–elastic peaks are found in U heavy–fermion systems [315] and can have a wide range of values for the product $\Gamma(0) \gamma$. The narrow quasi–elastic response can also be interpreted as the response of a gas of heavy quasi–particles in a very narrow band. The $q$ dependent contributions may signify fluctuations associated with long–ranged order or competing types of short–ranged order. In particular, the quasi–particle contribution to the susceptibility should show up at very low temperatures as a narrow quasi–elastic peak at small energy and momentum transfers. The intensity of the peak should be proportional to the quasi–particle weight but may be significantly reduced by spin–orbit scattering. For the cerium heavy–fermion compounds [229,230,232–234], the higher energy spectra also show inelastic peaks due to crystal field excitations. As seen in Fig. 10.48, the localized crystal field excitations can be reasonably described by the single impurity Anderson model.

Inelastic neutron scattering experiments on UPt$_3$ show the existence of a local relaxational component to the response which has a width of $\Gamma = 9$ meV [316]. The experimental data are shown in Fig. 10.49. The $q$ dependence is associated with three different types of magnetic correlations. Long wavelength ferromagnetic $(0,0,0)$ fluctuations gradually start developing below 150 K [317] and show a $q$ dependent energy width $\Gamma(q) \propto q$. These
fluctuations are similar to paramagnons since, for $q \to 0$ fluctuations, one expects

$$1 - U \ Re \chi_0(q; \omega) \sim 1 - U \rho(\mu) + O\left(\frac{q}{k_F}\right)^2$$

(10.175)

and

$$Im \chi_0(q; \omega) \sim \frac{\pi}{4} \rho(\mu) \left(\frac{\hbar \omega k_F}{\mu q}\right).$$

(10.176)

Within RPA, this behavior of the quasi-particle susceptibility produces the pre-critical fluctuations appropriate to a damped, but conserved, order parameter. The paramagnon fluctuations could be responsible for the $T^3 \ln T$ term observed in the specific heat and the value of the large Korringa ratio \[279, 280\]. In addition to the $(0,0,0)$ fluctuations, there are two types of antiferromagnetic modes in the spectrum. A quasi-elastic peak starts developing below $T = 30$ K centered at momentum transfers of $(0,0,1)$ and is characterized by a large energy width $\Gamma \sim 5$ meV \[318, 319\]. This signifies the presence of a rapidly changing short-ranged magnetic order in which the two uranium ions in the unit cell are antiferromagnetically coupled. This produces an antiferromagnetic correlation between the spins along the $c$ axis and a ferromagnetic correlation between the spins in the basal plane. The intensity of the inelastic peak decreases as $q$ is varied away from $(0,0,1)$. The width of the peak $\Delta q \sim \xi^{-1}$ provides a measure of the correlation.
length $\xi$. The anisotropy of the correlation length in UPt$_3$ suggests that fluctuating in–plane ferromagnetic correlations are present for temperatures as large as $T = 100$ K. The second type of antiferromagnetic fluctuations is associated with a wave–vector of ($\frac{1}{2}, 0, 1$) which develops at $T = 18$ K and peaks at a frequency of the order of 0.2 meV. Magnetic ordering occurs at this wave–vector below the critical temperature of $T_N = 5$ K, as evidenced by the development of magnetic Bragg peaks at ($\frac{1}{2}, 0, 1$), since the magnetic Bragg peak intensities are (apart from the temperature dependent Debye–Waller factor) proportional to the square of the sub–lattice magnetization. The magnetic moments are in the basal plane of the hexagonal structure and are aligned parallel to the propagation vector $\mathbf{Q} \equiv (\frac{1}{2}, 0, 0)$. The magnitude of the ordered moments found through neutron diffraction experiments are anomalously small. The measured ordered moment only attain the value of 0.02 $\mu_B$ per U ion just above the superconducting transition temperature $T_c$ [291]. The temperature dependence of the intensity of the magnetic Bragg peak of UPt$_3$ is shown in Fig. 10.50. The temperature dependence of the magnitude of the sub–lattice magnetization $M_{\mathbf{Q}}(T)$ follows the scaling law

$$|M_{\mathbf{Q}}(T)| \propto (T_N - T)^\beta$$  \hspace{1cm} (10.177)

for $T_N > T$, where $\beta \sim 0.5$. The value of the critical exponent is not consistent with the values expected for three dimensional ordering of localized magnetic moments. Similar values of $\beta$ are also found in other systems with anomalously low magnetizations such as URu$_2$Si$_2$ at ambient pressure. The critical exponents $\beta$ found for other magnetically ordered heavy–fermion systems with larger moments such as UNi$_2$Al$_3$, UPd$_2$Al$_3$ and U$_2$Zn$_{17}$, have
Fig. 10.50. (a) The temperature dependence of the elastic scattering intensity for UPt$_3$ at $q = (\frac{1}{2}, 0, 1)$. For purposes of comparison, (b) shows the temperature dependence of scattering with energy transfers of 85 µeV at $q = (0.52, 0, 0.99)$. [After Aeppli et al. (1988), [320]]

values close to 0.35 which are within the range expected for three-dimensional ordering of localized moments. For comparison, we show the temperature dependence of the magnetic Bragg peak intensity of UPd$_2$Al$_3$ in Fig. 10.51. The correlation lengths associated with the Bragg peaks of UPt$_3$ remain finite above and below $T_N$, and are of the order of 250 – 500 Å [320]. As the cross-section for elastic Bragg scattering is proportional to the energy conserving Dirac delta function $\delta(\omega)$, measurements of the elastic Bragg peaks involve windows of energy transfers which includes the point $\omega = 0$. Thus, the Bragg intensity also contains contributions from low-energy critical scattering, which have finite correlation lengths. Since the Bragg peaks were observed to have finite correlation lengths, questions are raised as to the nature of the ordering whether it is quasi-static short-ranged ordering, or whether it is long-ranged ordering that is interrupted by the presence of defects [321]. Muon spin resonance experiments confirmed the presence of magnetic ordering at $T_N \sim 5$ K [290, 322]. As the temperature is reduced from just above the superconducting transition temperature, the intensity of the antiferromagnetic Bragg peaks shows a sudden change of slope as it starts
to decrease. This indicates that the antiferromagnetic ordering coexists and competes with the superconductivity [323].

Inelastic neutron scattering experiments on UBe$_{13}$ [324, 325] at $T \sim 10$ K show an approximately $q$ independent relaxational paramagnetic response with a large quasi-elastic width $\Gamma = 14$ meV. The approximate $q$ independence of the inelastic scattering cross-section is indicative of the localized nature of the magnetic fluctuations. At energy transfers less than 2 meV [315], there is another roughly $q$ independent quasi-elastic component to the spectrum, of width $\Gamma \sim 1.6$ meV at $T = 1.0$ K, which decreases to 1.0 meV at $T = 0.6$ K. If these smaller values of $\Gamma(0)$ are combined with the specific heat coefficient $\gamma$, the product $\gamma \Gamma(0)$ has a value of 1.7 which is closer to the values found for Ce heavy-fermion compounds. Antiferromagnetic like correlations are apparent in the quasi-elastic spectrum at momentum transfers $(\frac{1}{2}, \frac{1}{2}, 0)$ below a temperature of 30 K [326], but no long-ranged magnetic order was found.

Neutron scattering experiments on URu$_2$Si$_2$ show an instability to an antiferromagnetically ordered state below $T_N = 17.5$ K with average ordered magnetic moments of only $\mu \sim 0.03 \mu_B$ [327] or 0.023 $\mu_B$ per U [328]. The value of the ordered moment increases when pressure is applied, becoming as large as 0.25 $\mu_B$ per U atom at $P = 1.3$ GPa [226]. The measured value of the critical exponent for magnetic order parameter is $\beta \sim 0.5$ at ambient pressure. However, for URu$_2$Si$_2$, the comparison of NMR and neutron diffraction experiments under pressure [225] indicate that magnetism only occurs in a small temperature dependent fraction of the sample volume and that, if the temperature dependence of the volume is accounted for, the critical exponent $\beta$ falls within the normal range. Initial reports suggested that the correlation length $\xi$ remained finite and was of the order 200 to 400 Å. Later, it was found that the correlation length is sample dependent and that the Bragg peaks of the highest quality samples were resolution limited [329].
The ordering found is consistent with a Type I antiferromagnetic structure in which the spins align parallel in planes perpendicular to the tetragonal c-axis and are anti-parallel between planes. Since “hidden ordering” has been suggested as the cause of the large specific heat jump at $T_N$, neutron diffraction measurements were performed using polarized beams and applied fields. However, these experiments show no evidence of the “hidden ordering” [298, 299].

At temperatures of the order of $T = 50$ K, the inelastic scattering spectrum of URu$_2$Si$_2$ [330] shows the presence of a broad quasi-elastic response of width $\Gamma \sim 6$ meV, suggesting that the spins have relaxational dynamics. Below the Néel temperature, the inelastic scattering spectra show that both sharp spin-wave like excitations and broad relaxational spin-fluctuations co-exist in the antiferromagnetic state. At $T = 1$ K, there are well defined dispersive spin-wave peaks along the $(1, q, 0)$ direction that have a minimum excitation energy of 1.8 meV at the Antiferromagnetic zone boundary [331] which is located at $q = 0$. The dispersion relation for these magnetic excitations is shown in Fig. 10.52. The longitudinal character of the spin-wave excitations, the Ising-like nature of the magnetic ordering, and the existence of a gap, all indicate that there is considerable anisotropy in the magnetic interactions at low temperatures. The spin-wave excitations are rapidly damped out above the Néel temperature $T_N$. The spectrum of magnetic fluctuations in the energy range between 4 and 12 meV appears to have a short correlation length, of the order of the lattice spacing, in that the intensity decreases slowly as $q$ is varied away from $Q = (1, 0, 0)$. The response in this energy range seems to be associated with Stoner excitations of the gas of heavy quasi-particles. Since URu$_2$Si$_2$ has a large magnetic anisotropy, and as it may play an important role in the formation of superconductivity, inelastic scattering measurements were made with the view of identifying the source of the anisotropy [332]. Although crystal-field like features were observed at the high energies of 49, 99 and 158 meV, these features had widths of 64, 36 and 89 meV, which are comparable with the splittings. This indicates that the $f$ states in URu$_2$Si$_2$ are much more strongly hybridized with the conduction band states than in the Ce heavy-fermion compounds, and perhaps, have a large mixed valent character. Like UPt$_3$, the intensity of the antiferromagnetic Bragg peak in URu$_2$Si$_2$ is diminished at the onset of the superconducting transition [333].

The inelastic neutron scattering spectra of cerium based heavy-fermion compounds are different from the uranium based heavy-fermion compounds in that they show clear evidence of crystal field splittings. An example is given by the inelastic neutron scattering spectra of CeAl$_3$ [234], which is shown in Fig. 10.53. Like the uranium compounds, the cerium compounds also show the existence of an almost $q$ independent quasi-elastic peak which develops at low temperatures, but in the low temperature limit, the widths
Fig. 10.52. The dispersion relation of a sharp magnetic excitation observed in URu$_2$Si$_2$. The dispersion relation is shown in the $(1, 0, \zeta)$, $(1 + \zeta, \zeta, 0)$ and $(1, 0, \zeta)$ directions. It should be noted that the dispersion relation does not go soft, as is expected for isotropic antiferromagnetic spin waves, but instead shows a gap. The existence of a gap is indicative of magnetic anisotropy. [After Broholm et al. (1991), [331]]

attain smaller values. For example, the width found in CeCu$_2$Si$_2$ [230, 334] is of the order of 1 meV, and is less than 0.5 meV for CeAl$_3$ [310].

In CeCu$_6$, the magnetic fluctuations exhibit an Ising–like anisotropy along the $b$ axis. Two different components of quasi–elastic magnetic scattering were identified [335, 336]. The first component which becomes apparent at temperatures below 10 K, has an almost $q$ independent quasi–elastic response with a width that follows a $\sqrt{T}$ temperature variation and has a residual width, $\Gamma(0)$, of the order of 0.4 meV. The second component consists of a narrower $q$ dependent quasi–elastic peak that starts developing below $T = 3$ K. For the Ce compounds, unlike the U compounds, the magnitude of the residual $q$ independent quasi–elastic width seems to correlate well with the large low temperature specific heat $\gamma$ values. The magnetic spectrum of CeCu$_6$ has a $q$ dependent component which shows a peak at a frequency of the order of 0.2 meV, and the $q$ dependence is indicative of incommensurate antiferromagnetic fluctuations with the pair of propagation vectors $(1 \pm \delta, 0, 0)$, where $\delta = 0.15$. The correlation length, $\xi$, in CeCu$_6$ was found to be anisotropic, and saturates below $T = 1.5$ K to values of the order of 4 Å along the $c$–axis and 10 Å along the $a$–axis [335], indicating that the order is definitely short–ranged. The temperature dependence of the various widths are shown in Fig. 10.54, and the temperature dependence of the correlation lengths are shown in Fig. 10.55. The $q$ dependent component of the total spectrum is
estimates to be much smaller than the local component by a factor of about 10.

The introduction of Au impurities substitutionally for Cu can drive paramagnetic CeCu$_{6-x}$Au$_x$ to an antiferromagnetic quantum critical point. The critical concentration is $x_c \approx 0.1$. The thermodynamic and transport properties of the disordered compound have anomalous temperature dependences in the vicinity of the quantum critical point. For example, the specific heat contains a $T \ln T$ term and the low temperature resistivity is linear in $T$ [337]. For $x > x_c$, the system has incommensurate order with three pairs of Bragg peaks located very near to the values $(1 \pm 0.15, 0, 0)$, identified in

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**Fig. 10.53.** The inelastic neutron scattering cross-section of CeAl$_3$. The spectrum shows a quasi–elastic contribution and a crystal field excitation. [After Goremychkin et al. (1999), [234]]
Fig. 10.54. The temperature variation of the single-site and inter-site contributions to the line-width $\Gamma(T)$, for CeCu$_6$. [After Rossat–Mignod et al. (1988), [335]]

the stoichiometric compound [338]. At the quantum critical point, the Bragg peaks broaden into ridges which connect into a “butterfly” shaped critical line [339]. The extended region of $q$ space were this type of critical scattering occurs is shown in Fig. 10.56. The anomalous critical exponents at the quantum critical point led Rosch et al. [340] to speculate that the magnetic fluctuations were two-dimensional, despite the underlying electronic system being three-dimensional. At the quantum critical point, the width of the magnetic response may be expected to vanish at $T = 0$, for an isotropic magnetic system, as the magnetic excitations soften. This has led Schröder et al. [341] to examine the energy dependence for $q$ on the critical “butterfly” and look for a $\hbar \omega/k_B T$ scaling, with the functional form

$$\text{Im } \chi(Q; \omega, T) \sim T^{-\alpha} g(\omega/T),$$  \hspace{1cm} (10.178)

where $g(\omega/T)$ is a universal scaling function. The scaling behavior is shown on a double logarithmic plot, for the best fit value of the exponent $\alpha = \frac{3}{4}$. The scaled data are shown in Fig. 10.57. This critical scaling behavior seems not to be just confined to the region of critical scattering since the static susceptibility also follows a modified Curie–Weiss form

$$\chi(T)^{-1} = \chi(0)^{-1} + a T^\alpha$$  \hspace{1cm} (10.179)
Fig. 10.55. The temperature variation of the correlation lengths $\xi(T)$ for intersite correlations along the a and c axes, for CeCu$_6$. [After Rossat-Mignod et al. (1988), [335]]

Fig. 10.56. The region of $q$ space where critical scattering occurs for Ce(Au$_x$Cu$_{6-x}$)$_6$. The region of critical scattering forms a "dog's bone" or "butterfly". The insert shows a resolution limited Bragg peak for $x = 0.2$ and $T = 50$ mK. [After Stockert et al. (1998), [339]]
with the exponent $\alpha = \frac{3}{4}$, as opposed to the Curie–Weiss value, $\alpha = 1$. Similar scaling has also been observed in the scattering cross–section of non–Fermi–liquid disordered compound UCu$_{5-x}$Pd$_x$ [342], with $x \sim 1$ and $x \sim 1.5$. However, in this case, the best critical exponent is $\alpha = \frac{1}{3}$ which indicates that the form of the scaling is non–universal. The magnetic response for $x \sim 1$ shows a $q$ dependence which is similar to that of the stoichiometric, antiferromagnetic, compound with $x = 0$. However, for $x = 1.5$, this $q$ dependence was not observed [343]. This was interpreted as signalling the cross–over from a quantum critical region to a quantum disorder region. The implications of these non–universal scaling results are not currently understood.

Neutron diffraction experiments on UPd$_2$Al$_3$ and UNi$_2$Al$_3$ show that these materials both undergo transitions to antiferromagnetic ordered phases [344]. UPd$_2$Al$_3$ orders magnetically at $T_N = 14.3$ K, and has a magnetic structure comprised of spins ferromagnetically aligned in the basal plane parallel to the $a$ direction. The sheets of ferromagnetically aligned spins are coupled antiferromagnetically with the sheets of spins in the neighboring planes. This arrangement corresponds to the wave–vector $Q = (0, 0, \frac{1}{2})$. The quasi–elastic peaks centered on the magnetic ordering vectors become resolution limited Bragg peaks in the antiferromagnetic phase. The Bragg peak intensities are consistent with the saturated magnetic moment having the magnitude of $0.85 \mu_B$ per U. The critical exponent $\beta$ is close to the value 0.326 expected for a three dimensional Ising system. The inelastic spectrum clearly shows the existence of a spin–wave mode with a peak position that disperses almost
linearly from an energy transfer close to zero at \( q = (0, 0, \frac{1}{2}) \) to 3 meV at \( q = (0, 0, 0.6) \). Thus, to within the experimental resolution, the spectrum shows the existence of dispersive spin–wave like excitations [345]. The line shape resembles an inelastic peak and, unlike conventional spin–waves, is subjected to significant broadening which is of the order of 1 meV. Higher resolution measurements show that as the temperature is lowered below \( T_N \), in addition to the peak due to the propagating spin–waves, a quasi–elastic peak with a \( q \) dependent width of about 0.5 meV can be resolved [346, 347].

At the superconducting transition of UPd\(_2\)Al\(_3\), the intensity of the \((0, 0, \frac{1}{2})\) Bragg peak shows that the sub–lattice magnetization undergoes a sharp but small ( 1% ) decrease with decreasing temperature. This indicates that superconductivity and magnetism coexist and compete [344, 348]. A superconducting gap was observed in the spin–wave spectrum below \( T_c \) [349]. The gap is marked by an inelastic peak at the magnetic Bragg vector which shows a sharp increase in intensity below \( T_c \). The gap switches on more rapidly than expected from the BCS theory and saturates at a value of \( \Delta(0) \geq 0.36 \) meV. This results in the ratio \( 2 \Delta(0) / k_B T_c \geq 4.6 \) instead of the value 3.5 expected from BCS theory [350]. The observation of the superconducting gap in the inelastic neutron scattering spectra makes UPd\(_2\)Al\(_3\) unique, and the observation of any \( q \) dependence should enable the symmetry of the order parameter to be obtained by direct methods.

Magnetic ordering in UNi\(_2\)Al\(_3\) is found to occur below a temperature \( T_N = 4.6 \) K. Neutron diffraction measurements [351] show incommensurate magnetic order with ordering wave vectors \( \mathbf{Q} = (\frac{1}{2} \pm \delta, 0, \frac{1}{2}) \) where \( \delta = 0.11 \) and the ordered moments are only 0.24 \( \mu_B \) per U. The critical exponent was found to have the value \( \beta \sim 0.345 \) as expected for a three dimensional \( x–y \) system. The widths of the Bragg peaks correspond to long coherence lengths of the order of 400 Å. The field dependence of the magnetic structure suggests that the magnetic moments align along the \( a \) direction in the basal plane and that the magnitude and sense of the moments are modulated [352]. Inelastic neutron scattering experiments [353] were unable to identify any spin–wave like excitations but did show a low–energy quasi–elastic peak which is strongly localized around the incommensurate wave vector. The energy width of the quasi–elastic peak decreases with decreasing temperatures, saturating to a value of the order of 0.6 meV. However, a more recent study [354] has investigated the spectrum at energy transfers in the range of 2 to 10 meV. It was found that there was a ridge of high intensity on a line segment near the incommensurate ordering vectors \((\frac{1}{2} \pm \delta, 0, \frac{1}{2})\) and there was also a well localized maximum around the wave–vector \((0, 0, \frac{1}{2})\). These peaks have widths of the order of 6 meV and start developing at temperatures below 80 K. In fact, for energy transfers greater than 0.5 meV ( \( \approx k_B T_N \) ), the intensity of the commensurate peak dominates over the incommensurate peak. That is, above this energy, the magnetic fluctuations of incommensurate UNi\(_2\)Al\(_3\) strongly resemble those of commensurate UPd\(_2\)Al\(_3\). In contrast to UPd\(_2\)Al\(_3\),
no superconducting gap was observable in the magnetic excitation spectrum of UNi$_2$Al$_3$ below the transition temperature.

10.4 Properties of the Superconducting State

10.4.1 Thermodynamic Properties

The Specific Heat

The entropy of the gas of quasi–particles is given by the formula

$$
S = -k_B \sum_{\sigma,k} \left[ (1 - f(E_{\sigma,k})) \ln[1 - f(E_{\sigma,k})] + f(E_{\sigma,k}) \ln[f(E_{\sigma,k})] \right]. \tag{10.180}
$$

Therefore, for unitary phases, the quasi–particle contribution to the specific heat is given by

$$
C_{qp}(T) = \frac{4}{T} \int_0^\infty dE \rho_{qp}(E) \left( E^2 \frac{\partial \Delta_0^2}{\partial T} \right) \left( -\frac{\partial f}{\partial E} \right) \tag{10.181}
$$

which involves the average of the temperature derivative of the square of the quasi–particle energy, evaluated at the position of the normal state Fermi surface. Since, in the mean–field approximation, the square of the gap has a finite slope for $T$ just below $T_c$ and is zero above, the specific heat has a discontinuity at $T_c$. In BCS theory, the magnitude of the jump has the value given by $3 \Delta_0(0) \rho(\mu) / T_c$. Thus, the value of the specific heat jump found in weak–coupling BCS theory when normalized by the normal state specific heat, is given by

$$
\frac{\Delta C(T_c)}{C(T_c)} = \frac{C_s - C_n}{C_n} = \frac{12}{7} \xi(3) = 1.426 \tag{10.182}
$$

This ratio is a measure of the quantity

$$
\frac{1}{2k_B^2 T_c} \left. \left( \frac{\partial \Delta_0^2(T)}{\partial T} \right) \right|_{T_c} \sim \left( \frac{\Delta_0(0)}{k_B T_c} \right)^2. \tag{10.183}
$$

The values of the specific heat jumps for strong coupling materials tend to be higher than the BCS value. For example the normalized jump for Pb is as large as 2.71. This trend is understood as being due to inelastic scattering processes [355, 356] which tend to suppress $T_c$ more than $\Delta_0(0)$. With the exception of UBe$_{13}$, the heavy–fermion superconductors have normalized specific heat discontinuities which either are of the same order as or are smaller than the BCS ratio. The values of the specific heat jumps show large variations which are mainly due to differences in sample quality. In UPt$_3$, the largest specific heat jumps are found in the samples with the sharpest transitions and highest $T_c$’s. In UPt$_3$ and URu$_2$Si$_2$, the transitions found are
usually broad, while UBe$_{1.3}$ shows the sharpest transition. The broadness of the transition initially found in UPt$_3$ was responsible for masking the double peak structure of the specific heat observed in higher quality samples. The deviation of the jump from the BCS value is indicative of anisotropic superconductivity as weak–coupling calculations indicate that the magnitude of the jump is diminished as the density of low–energy quasi–particle states increases. Thus, for example, the normalized specific heat jumps for the pristine BW, ABM and polar triplet states are, respectively, calculated as $\frac{\gamma_{\text{BW}}}{\xi(3)} \sim 1.426$, $\frac{\gamma_{\text{ABM}}}{\xi(3)} \sim 1.188$ and $\frac{\gamma_{\text{polar}}}{\xi(3)} \sim 0.792$, and decrease along with $T_c$ as the concentration of non–magnetic impurities is increased. The temperature dependence of the specific heats for various $p$–wave superconducting phases are shown in Fig. 10.58. In heavy–fermion superconductors, which generally are type II superconductors, the jump in the specific heat occurs at lower temperatures when magnetic fields, $H$, are applied. The jump marks the instability of the normal state to a vortex state. The relation between the temperature and field provides the temperature dependence of the upper critical field $H_{c2}(T)$. A $\lambda$ like anomaly is expected to occur in the specific heat at a lower temperature where the applied field $H$ is equal to the lower critical field $H_{c1}(T)$. At this temperature, the usual Abriksosov magnetization–field relation has an infinite slope which implies a similar temperature variation of the entropy, and produces the $\lambda$ anomaly. Good examples of this second anomaly are found in V and Nb superconductors [357,358].

**Low Temperatures**

The low–energy power law energy dependence of the quasi–particle density of states could be expected to show up in power law temperature dependence of the low temperature electronic specific heat, for $T \ll T_c$. For these temperatures, the order parameter is expected to have saturated, and so then, if one considers the Fermi liquid as being well formed, the quasi–particle contribution is given by

\[
C_{qp}(T) = \frac{4}{T} \int_0^\infty dE \, \rho_{qp}(E) \, E^2 \left( -\frac{\partial f}{\partial E} \right). \tag{10.184}
\]

This yield an exponentially activated behavior of the specific heat, $C_{qp}(T) \sim 9.17 \, \gamma_0 \, T \, \exp[-\Delta_0 / k_B T]$, for states like the BCS or BW states which have no nodes; a $T^3$ variation for the low temperature specific heat in the ABM phase with isolated nodes and a $T^2$ variation for the polar ($p_\pi$) or $d_{z^2-x^2-y^2}$ phase with lines of nodes. However, the experimentally determined low temperature specific heats of the superconducting heavy–fermion uranium compounds are described by

\[
C(T) = \gamma_s \, T + \epsilon_s \, T^n, \tag{10.185}
\]

More precisely, assuming a separable pairing interaction, the normalized specific heat jump yields a measure of the angular variation of the gap over the Fermi surface. It is equal to the BCS value of the discontinuity times the ratio of the square of the second moment of the gap to the fourth moment.
Fig. 10.58. The temperature dependent specific heat normalized to the normal state specific heat at $T_c$ calculated for various $p$-wave superconducting phases. The magnitude of the normalized discontinuity at $T_c$ decreases from $\approx 1.4$, to $1.2$ to $0.8$ along the series BW, ABM and polar. The low temperature specific heat shows an exponential variation for the BW state, whereas the low temperature specific heats of the ABM and polar phases show power law temperature variations which are consequences of the types of nodes in the order parameters

where $\gamma_s$ is sample dependent. The residual $\gamma_s$ has often been attributed to either the existence of a normal component, or due to a gapless phase caused by pair breaking impurities. For example, in UPt$_3$ the coefficient of the residual linear $T$ term takes values between 265 and 56 mJ mole$^{-1}$ K$^{-2}$ depending on sample quality [14]. This suggests that between $50\%$ and $16\%$ of the normal state Fermi surface is ungapped for these samples. The value of the exponent $n$ is 2 for UPt$_3$, whereas $n = 3$ for UBe$_{13}$ and UPd$_2$Al$_3$. The specific heat of URu$_2$Si$_2$ shows a quadratic temperature variation [359], and the smallest $\gamma_s$ value reported is 4 mJ mole$^{-1}$ K$^{-2}$ and the largest is 13 mJ mole$^{-1}$ K$^{-2}$. The smaller magnitude of the ratio $\gamma_s/\gamma$ for URu$_2$Si$_2$ is perhaps not surprising since it has been estimated that about $30\%$ of the Fermi surface remains ungapped below the 17.5 K transition. In CeCu$_2$Si$_2$, the temperature dependence of the specific heat below $T_c$ is non-exponential, and can be fitted via a $T^2$ variation close to the critical temperature but shows a $T^3$ variation at low temperatures down to 50 mK. A residual value of $\gamma_s$ of the order of 24 mJ mole$^{-1}$ K$^{-2}$ has been reported [360]. This number suggests that only $4\%$ of the original Fermi surface is ungapped in the superconducting state of CeCu$_2$Si$_2$. The values of the exponents, $n$, suggests that there are nodes in the superconducting gap, however, the pair breaking effects of impurities may alter the temperature dependence [153–155] and may also lead to a gapless phase. This is consistent with the observation that materials with the broad-
est transitions tend to have the largest values of $\gamma_s$. As the heavy–fermion superconductors may be in the vicinity of quantum critical point, the Fermi liquid may not have been fully formed before the superconducting transition occurs as is true for UBe$_{13}$, and as the specific heat provides a measure of the density of all low–energy excitations and not just quasi–particles, it may prove difficult to disentangle the various factors which affect the temperature dependence of the specific heat.

**The Critical Fields**

The thermodynamic critical field $H_c$ of a superconductor is determined by equating the energy of the magnetic field to the difference in free energies between the superconducting and normal states

$$V_o \frac{H_c^2(T)}{8\pi} = F_n - F_s,$$

(10.186)

where $V_o$ is the volume. At $T = 0$ this reduces to the condensation energy of the superconducting state

$$V_o \frac{H_c^2(T)}{8\pi} = U_n - U_s = \frac{1}{2} \rho(\mu) \int \frac{d\Omega}{4\pi} \text{Trace} \Delta(k)\Delta^\dagger(k).$$

(10.187)

Here, $\rho(\mu)$ is the single–particle density of states at the Fermi energy and $\Delta(k)$ is the gap function. For an $s$–wave superconductor at finite temperatures $F = U - TS$ with $U_n - U_s = \frac{1}{2} \rho(\mu) \Delta_0^2(T)$ and the temperature dependent gap is determined from

$$\frac{1}{\rho(\mu)V} = \int_0^{\hbar \omega_c} d\xi \frac{\tanh (E/2k_B T)}{E},$$

(10.188)

where $-V$ is the potential for scattering a pair of electrons (assumed constant in BCS theory), $\omega_c$ is a cutoff frequency (usually the Debye frequency), $E = \sqrt{\xi^2 + \Delta_0^2}$, and the entropy of the superconducting state is

$$S_s = -2k_B \rho(\mu) \int_0^{\hbar \omega_c} d\xi \left[ f(E) \ln f(E) + (1 - f(E)) \ln (1 - f(E)) \right],$$

(10.189)

where $f(E) = 1/(e^{E/k_B T} + 1)$.

When solved numerically, in either the strong or weak coupling limit, the solution of the above equations differs from

$$H_c(T) = H_c(0) \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$$

(10.190)

by no more than a few percent. Meissner flux expulsion and zero resistivity disappear at $H_c$ and the normal state is recovered. (It is interesting to note...
that Eqn. (10.190), a good approximation to the BCS result, follows from a two–fluid model of superconductivity proposed by Gorter and Casimir in 1934. In this model the free energy of the normal state is taken to be \(-\frac{1}{2}\gamma T^2\) and the free energy of the superconducting state is a constant [361].

In a type–I superconductor the only critical field is \(H_c\) discussed above. In a type–II superconductor, quantized flux vortices appear in fields greater than the lower critical field \(H_{c1}\), and superconductivity persists to fields as high as the upper critical field \(H_{c2}\) where the normal cores of the vortex lattice overlap and the zero resistance state is destroyed. The creation of the vortex state becomes energetically favorable when the Ginzburg–Landau parameter \(\kappa > 1/\sqrt{2}\) \((\kappa = \lambda/\xi)\) where \(\lambda\) is the penetration depth and \(\xi\) is hereafter the coherence length. When \(\kappa \gg 1\) (an appropriate limit for the heavy–fermion superconductors) the Ginzburg–Landau equations can be solved to give

\[
H_c = \frac{\Phi_o}{2\sqrt{2\pi\mu_o}\lambda\xi},
\]

\[
H_{c1} = H_c \frac{\ln \kappa}{\sqrt{2}\kappa} = \frac{\Phi_o}{4\pi\mu_o\lambda^2} \ln \left(\frac{\lambda}{\xi}\right),
\]

and \(H_{c2} = \sqrt{2} \kappa H_c = \frac{\Phi_o}{2\pi\mu_o\xi^2}\).

Here, \(\Phi_o\) is the flux quantum (similar results for anisotropic systems are summarized elsewhere [362]). In the high \(\kappa\) limit generally appropriate for the heavy–fermion superconductors, \(H_c\) is very nearly the geometric mean of \(H_{c1}\) and \(H_{c2}\). In fact, there are three Ginzburg–Landau parameters which depend on \(T, l/\xi\) (where \(l\) is the mean free path), and the degree of anisotropy of the impurity scattering. However, the various \(\kappa_i\) differ from \(\kappa\) by no more than 20% [363], and we will not pursue the matter here.

Many early theories of the upper critical field focused on the maximum attainable field associated with a single limiting factor. An example of such a limiting factor, frequently encountered in the heavy–fermion superconductors, is the field dependence of the normal state free energy caused by the coupling to the paramagnetic spins. Since the spin susceptibility of spin–singlet superconductors vanishes at \(T = 0\), the Pauli limiting field \(H_p(0)\) is defined as the field at which the free energy of the normal state with spin susceptibility \(\chi_n\) equals the condensation energy of the superconducting state. At \(T = 0\), the definition takes the form

\[
\frac{1}{2} \chi_n H_p^2(0) = \frac{1}{2} \rho(\mu) \Delta_0^2(0).
\]

\(H_p\), sometimes known as the Chandrasekhar [364] or Clogston [365] limit, can be significantly enhanced when spin–orbit coupling is strong. At \(T = 0\)

\[
H_{p,so}(0) = \left(\frac{\hbar}{6\lambda_{so}\Delta(0)}\right)^{1/2} H_p(0),
\]
where $\lambda_{so}$ is the spin–orbit coupling parameter. Since the zero temperature limit of the spin susceptibilities of spin–triplet superconductors are generally expected to be either non–zero or anisotropic, the upper critical field may be expected to exceed $H_p(0)$ in spin–triplet phases. In particular, for a spin–triplet superconductor, a field applied parallel to the direction of the Cooper pairs spin will not be subject to the Pauli limit but fields with components in the perpendicular directions will produce pair breaking [366].

Perhaps the most commonly used and successful framework to interpret $H_{c2}(T)$ measurements on “classic” Type II superconductors is that developed by Werthamer, Helfand, Hohenberg, and Maki (WHHM) [367, 368]. WHHM solved the Ginzburg–Landau equations incorporating both orbital and spin paramagnetic effects in addition to both nonmagnetic and spin–orbit scattering. The resulting $H_{c2}$ curves are qualitatively similar to the shape of Eqn. (10.190) featuring a linear temperature dependence below $T_c$ that gently rolls over to a constant as $T \to 0$ (in other words, $H_{c2}(T)$ exhibits negative curvature or none at all). Since these predictions, which work so well with classic Type II superconductors, generally fail (except in the broadest terms) with heavy–fermion superconductors, we will not pursue this approach here but refer the reader to the overview and compilation of formulas presented by Orlando et al. [369]. Strong coupling can also cause significant deviations from the behaviors discussed above and we refer the reader to the overview of Carbotte [124]. Critical field anisotropy can originate from an anisotropic Fermi surface (sometimes characterized by an effective mass tensor [362]), an anisotropic order parameter, or magnetism for example.

Specific predictions for the upper critical fields resulting from anisotropic order parameters (or combinations thereof) have been made by a number of authors. In many cases, such as the $p$–wave ABM state for example [370,371], these order parameters lead to a characteristic anisotropy of $H_{c2}$ even though the temperature dependence remains similar to that of the WHHM model. In other cases the temperature dependence is also affected, and can result in the positive curvature which is so inconsistent with the WHHM model [372, 373]. A good overview of these issues can be found in the review article by Sigrist and Ueda [155].

The appearance of a non–uniform superconducting state, independently predicted in the mid–60’s by Fulde and Ferrell [374] and Larkin and Ovchinnikov [375], below $T/T_c \approx 0.55$ and in fields near $H_{c2}$ has sometimes been invoked to explain the unusual shapes of the upper critical fields exhibited by the heavy–fermion superconductors. The so–called FFLO state is one in which the internal magnetic field breaks a number of the spin–singlet Cooper pairs, and produces a uniform flow of the condensate. This state is stabilized when the current of the Cooper pair condensate is compensated by a counter flow of the quasi–particle gas. This FFLO state is suppressed by impurities and results in an additional first–order phase transition to the (relatively more uniform) vortex lattice state [376].
Many features of the models discussed above are consistent with the heavy electrons themselves entering the superconducting state. For example, standard thermodynamics shows that \[ \left( \frac{\Delta C}{T} \right) \bigg|_{H_c^2(T)} = \left( \frac{\partial H_{c2}}{\partial T} \right)^2 \left[ \left( \frac{\partial M}{\partial H} \right)_s - \left( \frac{\partial M}{\partial H} \right)_n \right] \].

Thus, the large initial slope of the upper critical field and the low values of \( T_c \) are related to the large effective masses of the electrons forming the Cooper pairs. Parameters characterizing the critical field curves of the heavy–fermion superconductors are collected in Table 10.11.

The upper critical field of UPt\(_3\) reflects the three underlying superconducting states meeting a tetra–critical point (at 0.39 K and 0.44 T) which manifests as a sharp kink in \( H_{c2}(T) \) when fields are applied along the \( c \)–axis. The anisotropy of \( H_{c2}(T) \) reverses sign near 0.2 K: above (below) this temperature \( H_{c2} \) is larger (smaller) with fields applied along the \( c \)–axis than with fields applied within the basal plane. There have been fewer measurements of the lower critical field of UPt\(_3\) owing, in part perhaps, to the difficulty of these measurements. All of the measurements are consistent with a sharp increase in slope near the transition between the lower temperature B phase and higher temperature A phase though the existence and size of the anisotropy is somewhat less certain. An increase in slope is consistent with the appearance of a second order parameter which would increase the condensation energy. A deeper discussion of the critical fields of UPt\(_3\) can be found in the recent review article by Joynt and Taillefer [378].

The upper critical field of the best single crystal samples of UBe\(_{13}\) shows a broad region of positive curvature setting in near \( T_c/2 \) which has been interpreted as evidence for the FFLO state discussed above [379,380]. Sharp features in \( H_{c2}(T) \) (or, more correctly, the irreversibility curve) of UBe\(_{13}\), suggesting additional phases in either the superconducting or normal state have been reported [381] but as yet there is no consensus on the existence of such features. An anisotropy consistent with lines of zeros for the gap function has been reported [382,383] but has not been confirmed [384]. Despite the unusual shape of the upper critical field, the lower critical field of a polycrystal sample of UBe\(_{13}\) exhibits the usual quadratic temperature dependence [385], however, we are unaware of any measurements on single crystals at this time.

In CeCu\(_2\)Si\(_2\), the upper critical field exhibits a broad, shallow maximum centered near 0.2 K the origin of which is uncertain but suggestions have included “(1) exchange–enhanced ‘polarization fields’ between (residual) Ce moments, (2) ‘Kondo–type’ pair breaking from these residual moments, and (3) competition between the (phonon–mediated) attraction and Coulomb repulsion between those slowly moving heavy–fermions whose velocity is already comparable to the velocity of sound” [22]. At low temperatures, the upper critical field with fields applied along the \( c \)–axis is about 20% larger than when they are applied along the \( a \)–axis. The size of this anisotropy decreases
monotonically as $T_c$ is approached. In earlier studies, the anisotropy vanished near $T_c$ near which the slopes of the critical field curves were equal [22]. More recently, however, a small anisotropy has been observed to exist very close to $T_c$ where the slopes vary from 23 T/K with fields along the a–axis to 18.5 T/K with fields along the c–axis [386]. The few measurements of the lower critical field of CeCu$_2$Si$_2$ show a short region of positive curvature just below $T_c$ [385, 387].

Table 10.11. The Superconducting parameters of some heavy fermion superconductors. Values separated by slashes characterize a–axis/c–axis anisotropy (∗ under pressure).

| Material       | $T_c$ (K) | $\Delta C(T_c)/C(T_c)$ | $H_{c2}(0)$ (T) | $-\frac{dH_{c2}}{dT}|_{T_c}$ (T/K) | $H_{c1}(0)$ (mT) | Refs.        |
|----------------|-----------|-------------------------|-----------------|------------------------------------|-----------------|-------------|
| UPe$^3$        | 0.55      | 1.0                     | 2.5 / 2.0       | 4.5 / 7.7                           | 3.0             | [378, 481, 498] |
| CeCu$_2$Si$_2$ | 0.69      | 1.27                    | 2 / 2.4         | 23                                 | 2.3             | [388, 481, 498] |
| UBe$_{13}$     | 0.9       | 2.5                     | 12              | 42                                 | 4.5             | [388, 481, 498] |
| URu$_2$Si$_2$  | 1.5       | 0.82                    | 13 / 3          | 4 / 14                             | 1.4             | [481, 498]     |
| UPd$_2$Al$_3$  | 2.0       | 1.2                     | 3.0 / 3.6       | 4.3                                | 1.0             | [481, 498]     |
| UNi$_2$Al$_3$  | 1.0       | 0.5                     | 1.5             | 1.4                                | 1.4             | [481, 498]     |
| CeRhIn$_5$     | 2.1*      | 0.36                    | 16              | 14                                 |                 | [57, 522]      |
| CeIrIn$_5$     | 0.4       | 0.76                    | 9.3 / 5.3       | 4.8 / 2.5                          |                 | [523]         |
| CeCoIn$_5$     | 2.3       | 4.5                     | 11.7 / 5.0      | 24.0 / 11.4                        | 2.5 / 9.5       | [523, 524, 526] |
| CeIn$_3$       | 0.18*     | 0.45                    | 3.2             |                                    |                 | [64, 530]     |
| CePd$_2$Si$_2$ | 0.52*     | 2                      | 13              |                                    |                 | [530, 532]    |
| CeRh$_2$Si$_2$ | 0.35*     | 0.35                    | 1.4             |                                    |                 | [68]         |
| CeCu$_2$Ge$_2$ | 0.7*      | 2                      | 11              |                                    |                 | [535]        |
| PrOs$_4$Sb$_{12}$ | 1.85   | 3                      | 2.2             | 1.9                                | 23              | [537, 541, 542] |
| U$_2$PtC$_2$   | 1.47      |                         | 9               |                                    |                 | [543]        |

10.4.2 Transport Properties

At sufficiently low temperatures, transport properties are determined by the properties of the quasi–particle excitations and, unlike thermodynamic properties, are essentially affected by scattering. If the temperature is so low that inelastic scattering from low–energy collective fluctuations is frozen out, then elastic impurity scattering may be expected to provide the dominant scattering mechanism. However, it is not appropriate to treat the impurity scattering in the Born approximation since it leads to a scattering time that has the same energy dependence as the quasi–particle density of states and which would lead to similar temperature dependences as in the normal state. This
is in contradiction to experimental observation. Hence, as pointed out by Pethick and Pines [156], it appears as if the impurity scattering is resonant.

**Thermal Conductivity**

The electronic contribution to the thermal conductivity can be calculated via linear response theory. The thermal conductivity can be expressed in terms of the heat flux correlation function. The thermal conductivity tensor $\kappa_{i,j}(T)$ can be written as the limit $\omega \to 0$ of the expression [390]

$$\kappa_{i,j}(T) = -\frac{1}{\hbar T} \left( \frac{\partial \text{Im} K_{i,j}^R(\omega)}{\partial \omega} \right)_{\omega=0}, \quad (10.197)$$

where

$$K_{i,j}^R(\omega) = \frac{\hbar^2}{8m^2} \int \frac{dE_1}{2\pi} \int \frac{dE_2}{2\pi} \frac{(E_1 + E_2)^2}{E_1 - h\omega - E_2 - i\delta} \left( f(E_2) - f(E_1) \right) \times \sum_k k_i k_j \text{Trace} \left( \text{Im} G(k; E_1) \rho_4 \text{Im} G(k; E_2) \rho_4 \right)_{\text{av}} \quad (10.198)$$

and where the Trace is over the matrix Green’s function $G(k; \omega)$ defined by Eqn. (10.86). This expression is to be averaged over the distribution of impurities. This type of analysis produces the standard result

$$\kappa_{i,j} = \frac{1}{T} \sum_{\sigma, k} v_i(k) v_j(k) \tau(E_k) E_k^2 \left( -\frac{\partial f}{\partial E_k} \right) \quad (10.199)$$

in which $v(k)$, $E_k$ and $\tau(E_k)$, respectively, are the quasi–particle velocity, the quasi–particle energy and the quasi–particle lifetime.

**Singlet Pairing**

For the case of isotropic singlet pairing and in the Born approximation, the rate of scattering of a quasi–particle from state $k$ to state $k'$ by non–magnetic impurities is given in terms of the quasi–particle density of states by

$$\frac{1}{\tau(E_k)} = \frac{1}{\tau_0} \frac{\rho_{\text{BCS}}(E_k)}{\rho(\mu)} \left( 1 - \frac{\Delta_0^2}{E_k^2} \right), \quad (10.200)$$

where the normal state scattering rate due to a concentration of randomly distributed non–magnetic impurities, $c_0$, is given by

$$\frac{1}{\tau_0} = \frac{2\pi}{\hbar} c_0 \rho(\mu) |U_0|^2. \quad (10.201)$$

This expression for the thermal conductivity of a superconductor was derived by O. Betbeder–Matibet and P. Nozi`eres, using a Boltzmann equation approach (O. Betbeder–Matibet and P. Nozières, Ann. Phys. (N.Y.) 51, 392 (1969)). This result is obtained when the self–energy due to impurity scattering is small compared with $k_B T$. 

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---
The quasi–particle velocity is defined by

$$v(k) = \frac{1}{\hbar} \frac{\partial E_k}{\partial k} = \frac{\hbar k}{m} \left( \frac{e(k) - \mu}{E_k} \right),$$

(10.202)

where the order parameter has been assumed to be approximately independent of the magnitude of $k$. Hence, the coherence factor in the expression for the quasi–particle lifetime $\tau(E_k)$ will cancel with a factor of

$$\left( \frac{e(k) - \mu}{E_k} \right)^2$$

(10.203)

in the expression for $v_i(k) v_j(k)$. On combining these expressions, and on replacing the sum over $k$ by integrals over the solid angle and the magnitude of $k$, one finds that the conductivity tensor is given by

$$\kappa_{i,j} = \frac{2 \tau_0}{T} \left( \frac{\hbar k_F}{m} \right)^2 \int d\Omega \int_{-\infty}^{+\infty} dE \rho BCS(E) E^2 \left( -\frac{\partial f}{\partial E} \right).$$

(10.204)

The integral over the solid angle $d\Omega$ causes the off–diagonal components of the tensor to vanish, and yields equal diagonal components. The tensor is given by

$$\kappa_{i,j} \approx \delta_{i,j} \frac{4 \tau_0}{3T} \left( \frac{\hbar k_F}{m} \right)^2 \rho(\mu) \int_{\Delta_0}^{\infty} dE E^2 \left( -\frac{\partial f}{\partial E} \right).$$

(10.205)

In this expression, the factor of the quasi–particle density of states is absent as we have used the Born approximation for the quasi–particle lifetime. On evaluating the integral at low temperatures, where $k_B T \ll \Delta_0$, one finds

$$\kappa_{i,j}(T) = \delta_{i,j} \frac{4 \tau_0}{3T} \left( \frac{\hbar k_F}{m} \right)^2 \rho(\mu) \Delta_0^2 \exp \left[ -\beta \Delta_0 \right].$$

(10.206)

Therefore, the quasi–particle component to the thermal conductivity tensor of a BCS superconductor is thermally activated and is isotropic.

For the case of anisotropic pairing, the Born approximation for the scattering rate is given in terms of the quasi–particle density of states by

$$\frac{1}{\tau(E_k)} = \frac{1}{\tau_0} \frac{\rho_{qp}(E_k)}{\rho(\mu)},$$

(10.207)

since the angular integration over the final state momentum $k'$ has caused the term in the coherence factor which is bi–linear in the order parameter to vanish. Since the cancellation between the coherence factor in the lifetime and the factors in the quasi–particle velocity does not occur for anisotropic
pairing, the quasi-particle contribution to the thermal conductivity tensor is given by

\[
\kappa_{i,j} = \frac{2}{T} \left( \frac{\hbar k_F}{m} \right)^2 \int \frac{d\Omega}{4\pi} \hat{k}_i \hat{k}_j \int_{-\infty}^{+\infty} de \left( e - \mu \right)^2 \rho^2(e) \rho_{qp}(E) \left( -\frac{\partial f}{\partial E} \right) \]

\[
= \frac{4}{T} \left( \frac{\hbar k_F}{m} \right)^2 \rho^2(\mu) \int \frac{d\Omega}{4\pi} \hat{k}_i \hat{k}_j \int_{|D(k)|}^{\infty} dE \frac{E}{\rho_{qp}(E)} \sqrt{E^2 - |D(k)|^2} \left( -\frac{\partial f}{\partial E} \right). \tag{10.208}
\]

On interchanging the order of the integrations, one obtains the result

\[
\kappa_{i,j} = \frac{4\tau_0}{T} \left( \frac{\hbar k_F}{m} \right)^2 \rho^2(\mu) \int \frac{d\Omega}{4\pi} \hat{k}_i \hat{k}_j \int_0^{\infty} dE E \frac{E}{\rho_{qp}(E)} \left( -\frac{\partial f}{\partial E} \right) I_{i,j}(E), \tag{10.209}
\]

where the factor \( I_{i,j}(E) \) describes the anisotropy, and is given by

\[
I_{i,j}(E) = \int \frac{d\Omega}{4\pi} \hat{k}_i \hat{k}_j \sqrt{E^2 - |D(\hat{k})|^2}. \tag{10.210}
\]

The integration only runs over the solid angles for which the argument of the square root is positive. Assuming the validity of this expression, one observes that there exists a possibility that the anisotropy of the thermal conductivity tensor may provide information about the locations of the nodes of the order parameter.

For illustrative purposes, we shall consider the \( d \)-wave order parameter with \( m = 1 \),

\[
D(\hat{k}) = \Delta_0 \sin 2\theta \exp[i\varphi]. \tag{10.211}
\]

This order parameter has a line of nodes in the equatorial plane and two isolated point nodes, one at each of the poles. Hence, the quasi-particle density of states is linearly proportional to \( E \) at low energies and is logarithmically divergent at \( E = \Delta_0 \). The thermal conductivity tensor only has diagonal components and is isotropic in the \( x-y \) plane. The anisotropy of the tensor is governed by the angular integrals

\[
I_{z,z}(E) = \frac{\Delta_0}{2} \int d\theta \sin \theta \cos^2 \theta \sqrt{\left( \frac{E}{\Delta_0} \right)^2 - \sin^2 2\theta},
\]

\[
I_{x,x}(E) = \frac{\Delta_0}{4} \int d\theta \sin \theta \sin^2 \theta \sqrt{\left( \frac{E}{\Delta_0} \right)^2 - \sin^2 2\theta}, \tag{10.212}
\]

where the integration only runs over the ranges of \( \theta \) where the argument of the square root is positive. For small \( E \), these integrals are proportional to \( E^4/\Delta_0^4 \) and \( E^2/\Delta_0^2 \) respectively. The differences in the behavior occurs because, at low energies, the line of nodes has more weight than the point
nodes and the factor of \( \cos^2 \theta \) in the \( z \) component of the tensor is limited to be smaller than \( E^2/4\Delta_0^2 \) while \( \sin^2 \theta \approx 1 \). Hence, for temperatures such that \( k_B T \ll 0.2 \Delta_0 \), one expects that \( \kappa_{z,z}(T) \propto T^3 \), while \( \kappa_{x,x}(T) = \kappa_{y,y}(T) \propto T \). The different temperature dependence of the components of the thermal conductivity tensor reflect the presence of the line of nodes in the equatorial plane.

Any anisotropic behavior of \( \kappa(T) \) is expected to be extremely difficult to observe experimentally, since a slight misalignment of the crystal, the presence of domains or grain boundaries etc., may cause the measured thermal conductivity to be dominated by the largest component of the tensor.

**Triplet Pairing**

In the case of triplet pairing, the quasi–particle contribution to the thermal conductivity can be written in a form analogous to the thermal conductivity for anisotropic singlet pairing. The tensor can be expressed as

\[
\kappa_{ij}(T) = \frac{\hbar^2 k_F^2}{m^2 k_B T^2} \rho(\mu) \int_0^\infty dE E \text{sech}^2 \frac{\beta E}{2} \tau(E) I_{i,j}(E),
\]

where \( \tau(E) \) is the scattering time and \( I_{i,j}(E) \) is given by

\[
I_{i,j}(E) = \int \frac{d\Omega}{4\pi} \frac{\hat{k}_i \cdot \hat{k}_j \sqrt{E^2 - |\vec{d}(\hat{k})|^2}}{\tau(E)}.
\]

In the BW phase, the order parameter is nodeless and so, the thermal conductivity is diagonal, isotropic and exponentially activated. Thus, the thermal conductivity in the BW phase is similar to the thermal conductivity of the BCS state.

For the ABM state, the low temperature thermal conductivity is anisotropic. As the magnitude of the order parameter varies as \( |\vec{d}(\hat{k})| = \Delta_0 \sin \theta \), the factor of \( k_F^2 \) in the diagonal components of the thermal conductivity tensor introduces an extra factor of \( E^2/\Delta_0^2 \) in the low–temperature limit of the transverse components compared with the longitudinal component. The longitudinal thermal conductivity is estimated as

\[
\kappa_(T) = \frac{\hbar^2 k_F^2}{k_B T^2} \rho(\mu) \int_0^\infty dE E E \text{sech}^2 \frac{\beta E}{2} \tau(E) \frac{E^3}{|\Delta_0|^2}.
\]

and the transverse components are estimated as

\[
\kappa_\perp(T) = \frac{\hbar^2 k_F^2}{k_B T^2} \rho(\mu) \int_0^\infty dE E \text{sech}^2 \frac{\beta E}{2} \tau(E) \frac{E^5}{|\Delta_0|^4}.
\]

In the Born Approximation, since \( \rho_{ABM}(E) \) varies as \( E^2 \) and thus \( \tau(E) \propto E^{-2} \), the longitudinal component of the thermal varies as \( \kappa_(T) \propto T \) whereas the transverse components vary as \( \kappa_\perp(T) \propto T^3 \).

For the polar state, where \( |\vec{d}(\hat{k})| = \Delta_0 \cos \theta \) which vanishes along the equatorial plane, the transverse and longitudinal components of the thermal
conductivity tensor are given by

$$\kappa_\perp(T) = \frac{\hbar^2 k_F^2}{k_B T^2 m^2} \rho(\mu) \int_0^\infty dE E \operatorname{sech}^2 \frac{\beta E}{2} \tau(E) \left| \frac{E^2}{\Delta_0} \right|$$  \hspace{1cm} (10.217)

and

$$\kappa_\parallel(T) = \frac{\hbar^2 k_F^2}{k_B T^2 m^2} \rho(\mu) \int_0^\infty dE E \operatorname{sech}^2 \frac{\beta E}{2} \tau(E) \left| \frac{E^2}{\Delta_0^3} \right|.$$  \hspace{1cm} (10.218)

In the polar state, the quasi–particle density of states is given by $\rho_{p_z}(E) \propto E$, hence $\tau(E) \propto E^{-1}$. Thus, one has $\kappa_\parallel(T) \propto T^3$ and $\kappa_\perp(T) \propto T$. It should be noted that the anisotropy in the $T$ dependence of $\kappa(T)$ is switched between the polar and the ABM states [391].

Since $\Delta_0 \gg k_B T$, the above results imply that the linear $T$ term will dominate the experimentally determined temperature variation of the thermal conductivity of either a polar or an ABM state. In general, a linear $T$ dependence is expected for states with either point or line nodes. Also, if the Lorentz number found in the normal state is constant, as is expected if impurities provide the dominant scattering mechanism, the thermal conductivity in the superconducting state should have a magnitude which is very similar to the normal state value. The above results were obtained using the Born approximation. However, it has been argued that, even in the normal state, it is not valid to treat impurity scattering within the Born approximation since the impurity scattering may be resonant, i.e., close to the unitarity limit.

If the impurity scattering is resonant and $k_B T \gg \hbar/2\tau$, then in the ABM phase one has $\tau(E) \sim \tau_0$, while $\tau(E) \propto E \ln^2 E$ in the polar phase. Thus, for resonant scattering, the leading $T$ dependences for the components of the thermal conductivity for the ABM phase are expected to be $\kappa_\parallel(T) \propto T^3$ and $\kappa_\perp(T) \propto T^5$. The polar phase has the opposite anisotropy to the ABM phase, however, additional factors of $\ln^3 T$ multiply the leading low–temperature powers of $T$. That is, for the polar phase, $\kappa_\parallel(T) \propto T^5 \ln^2 T$ and $\kappa_\perp(T) \propto T^3 \ln^2 T$. In general, it is expected that for strong scattering by dilute impurities such that the T–matrix approximation is valid [157, 392], the orientationally averaged thermal conductivity $\kappa(T)$ should follow a $T^3$ law if the order parameter has point nodes or should follow a $T^2$ law if the order parameter has line nodes.

However, the resonant impurity scattering may be sufficiently large to cause the superconducting quasi–particle density of states to be finite at zero energy. In this case, it has been shown [394] that the low–energy superconducting quasi–particles may be strongly localized, even when the normal state quasi–particles are not. This results in a universal expression for the d.c. limit of the electrical conductivity of the superconducting state which is finite and independent of the disorder. As a consequence, for $k_B T \ll \hbar/2\tau$, a Wiedemann–Franz like relation holds [395]. This relation shows that, in the very low temperature limit, the superconductor’s thermal conductivity $\kappa(T)$
should also be linear in $T$, irrespective of the node structure. Furthermore, the largest component of $\kappa_{i,j}(T)$ can also be independent of impurity scattering for certain types of order parameter \[395\]. These results can be understood by recognizing that the effect of strong impurity scattering is to randomize the Fermi surface, thereby acting to restore its approximate spherical symmetry.

The electronic contribution to the thermal conductivity of UBe$_{13}$ does not follow the exponentially activated law expected from BCS theory but shows a $T^2$ variation in the superconducting state at relatively high temperatures (between 0.8 and 0.1 K) which could be indicative of lines of nodes in the order parameter \[28\]. However, this assignment is contrary to the assignment of point nodes made on the basis of the $T^3$ variation observed in the specific heat. Experiments on some samples show that, below 100 mK, $\kappa(T)$ varies linearly with $T$

$$\kappa(T) = \alpha_s T ,$$  \hspace{1cm} (10.219)

where $\alpha_s = 0.03$ mW K$^{-2}$cm$^{-1}$ \[268\]. The temperature dependence of $\kappa$ for the two different temperature regimes found in this sample of UBe$_{13}$ are shown in Fig. 10.59. However, other samples do not show any noticeable linear temperature dependences \[396\]. This seems to indicate that the thermal conductivity is extremely sensitive to the quality of the sample.

The temperature dependence of the thermal conductivity of UPt$_3$ also does not follow an exponential activation law but has a temperature variation which can be fit by the sum of a $T$ and a $T^2$ term \[29, 397, 398\]

$$\kappa(T) = \alpha_s T + \beta_s T^2 .$$  \hspace{1cm} (10.220)

The value of the coefficient of the linear $T$ term, $\alpha_s$, was found to vary from sample to sample, varying from 0.55 to 12 mW K$^{-2}$ cm$^{-1}$. The magnitude of the coefficient $\beta_s$ of the $T^2$ term in UPt$_3$ can be as large as 60 mW K$^{-3}$ cm$^{-1}$ \[398\] which is two orders of magnitude greater than the corresponding coefficient in UBe$_{13}$. The strength of the $T^2$ term in the $\kappa(T)$ of UPt$_3$ is also much larger than the corresponding term found from the $\kappa(T)$ of CeCu$_2$Si$_2$ \[399\], for which $\beta_s \sim 1.8$ mW K$^{-3}$ cm$^{-1}$ and $\alpha_s \sim 0.28$ mW K$^{-2}$ cm$^{-1}$. Although an anisotropy of $\kappa(T)$ was detected in UPt$_3$ \[400\], the anisotropy is fully developed in the normal state and $\kappa(T)$ becomes more isotropic for temperatures below the second superconducting transition. An analysis of the measurements favors an order parameter with a form similar to $Y^2_1(\theta, \phi)$ but did not conclusively identify the symmetry of the gap.

The lack of agreement with expectations based on simple quasi–particle theories and elastic impurity scattering is perhaps not surprising, since the validity of the quasi–particle description of the normal state of both UBe$_{13}$ and CeCu$_2$Si$_2$ is questionable.

**Ultrasonic Attenuation**

Measurements of the ultrasonic attenuation should allow the temperature dependence and the anisotropy of the gap to be determined. Within BCS
Fig. 10.59. The temperature dependence of the thermal conductivity $\kappa$ of UBe$_{13}$, at low temperatures. The dashed line represents a possible linear term $\kappa(T) = \alpha_s T$. The insert shows the temperature dependence of $\kappa$ in a wider temperature range which extends up to $T_c$. [After Ravex et al. (1987), [268]]

Fig. 10.60. The temperature dependence of the attenuation rate for longitudinal and transverse sound in UPt$_3$. [After Müller et. al (1986), [405]]
theory, and even with s-wave pairing, the attenuation coefficients for longitudinal and transverse sound are different. This difference occurs since a longitudinal sound wave merely produces a time-dependent scalar potential which acts on the electrons, whereas a transverse sound wave produces a transverse electromagnetic field and hence, is subject to the Meissner effect. The Meissner effect has the effect of reducing the coupling strength between the electrons and the transverse phonons and, therefore, reduces the transverse attenuation rate just below the superconducting transition [401, 402]. This mechanism is held to be responsible for an almost discontinuous drop in the attenuation rate for shear waves in Al [403] and In [404] at $T_c$. Below the transition temperature, the evolution of the superconducting gap leads to a further reduction of the attenuation rate. This behavior is in direct contrast with the ultrasonic attenuation of the heavy-fermion superconductors UPt$_3$ [405–407], UBe$_{13}$ [26] and URu$_2$Si$_2$ [408], where peaks have been found in the ultrasonic attenuation just below $T_c$.

A sharp peak in the longitudinal attenuation coefficient was observed in UBe$_{13}$ in the form of a $\lambda$–like anomaly at a temperature just below the superconducting transition temperature of 0.8 K [26]. A similar sharp $\lambda$–like peak for the attenuation of longitudinal sound waves in UPt$_3$ was found at a temperature of about 500 mK [405]. A less pronounced and more rounded peak was also seen in the attenuation of transverse sound waves in UPt$_3$ [406, 407]. The peak in URu$_2$Si$_2$ [408] is of the form of a rounded $\lambda$–like anomaly and has a maximum at a temperature of $\sim$ 1.25 K, which is below the superconducting transition $T_c$ of 1.35 K. Initially, it had been speculated that these peaks have their origin in the collective modes of the superconducting order parameter, similar to the collective modes observed in $^3$He. However, in this case, the analogy with $^3$He is flawed. Since the crystals do not posses continuous rotational symmetries, but only have the discrete rotational symmetries contained in their point groups, the collective excitations are not Goldstone modes. If spin–orbit scattering is strong in these U compounds, the frequencies of the collective modes of the order parameter could have magnitudes similar to the superconducting gaps. Furthermore, these collective modes are only expected to be well defined [130, 409] at very low temperatures in very clean materials. Since the peaks in the attenuation coefficient occur at temperatures just below the critical temperatures, and since there appears to be a residual zero energy density of states due to impurity scattering, the collective modes are expected to be over–damped, therefore, this explanation seems unlikely.

An alternate viewpoint was provided by Coffey [410], who related the peak in the attenuation to the enhanced quasi–particle masses which makes the velocity of sound comparable to the Fermi velocity. In this picture, the conductivity enters the expression for the longitudinal attenuation rate, thereby producing a screening of the electron–phonon coupling. As in the normal state conductivity, the mass enhancement factor produces a sharp low–frequency Drude peak in the conductivity. Although this effect is
also predicted for a BCS state, it is stronger in anisotropic superconducting states where the low-energy quasi-particle density of states is finite, and so, the screening is more effective.

**Low Temperatures**

As a precursor to the discussion of the anisotropy in \( \alpha_q(T) \), we shall first examine the ultrasonic attenuation in an ordinary singlet superconductor. For a singlet superconductor, the attenuation rate is approximated by the Fermi Golden Rule expression

\[
\alpha_{q,i} = 2\pi|\lambda_{q,i}|^2 \sum_{k, \sigma} \left( 1 + \frac{(e(k) - \mu)(e(k + q) - \mu) - D(k)D(k + q)}{E_kE_{k+q}} \right) \\
\times (f(E_k) - f(E_{k+q}))\delta(E_{k+q} - E_k - \hbar\omega_{q,i}) ,
\]

where \( \lambda_{q,i} \) is the electron–phonon coupling strength, and \( \omega_{q,i} \) is the frequency of a phonon with wave-vector \( q \) and polarization \( i \). The summation over \( k \) can be separated into an integral over the magnitude of \( k \) (or \( e(k) \)) and an integral over the polar angle, \( \theta \), defined with respect to \( q \). For an s-wave superconductor, the angular integral can be replaced by an integral over the magnitude of \( e(k + q) \) where the range of integration runs between \( e(k - q) \) and \( e(k + q) \). The range of this transformed integral is shown in Fig. 10.61.

Conservation of energy \( E_{k+q} = E_k + \hbar\omega_{q,i} \) demands that the only \( k \) values that contribute to the attenuation are those which are close to the equatorial plane of the Fermi surface, if \( v_F > c \) and \( k_F > q \), as shown in Fig. 10.62. Since the term in the coherence factor proportional to \( e(k + q) - \mu \) is anti-symmetric under the integration, it vanishes, thereby yielding the expression

\[
\alpha_{q,i} = \frac{m^2}{\pi q\hbar^2} |\lambda_{q,i}|^2 \int_0^\infty \frac{dE_k}{e(k-q)} \int_{e(k-q)}^{e(k+q)} \frac{dE_{k+q}}{E_kE_{k+q}} \left( 1 - \frac{D(k)D(k + q)}{E_kE_{k+q}} \right) \\
\times (f(E_k) - f(E_{k+q}))\delta(E_{k+q} - E_k - \hbar\omega_{q,i}) ,
\]

which, since \( \omega_{q,i} \) is small, simplifies to

\[
\alpha_{q,i} = \frac{m^2}{\pi q\hbar^2} |\lambda_{q,i}|^2 \int_0^\infty \frac{dE_k}{e(k-q)} \int_{e(k-q)}^{e(k+q)} \frac{dE_{k+q}}{E_kE_{k+q}} \left( \frac{e(k) - \mu}{E_k} \right)^2 \\
\times \left( -\frac{\partial f(E_k)}{\partial E_k} \right) \delta(E_{k+q} - E_k - \hbar\omega_{q,i}) \\
= \frac{m^2}{\pi q\hbar^2} |\lambda_{q,i}|^2 \int_{\Delta_0}^{\infty} dE_k \left( -\frac{\partial f(E_k)}{\partial E_k} \right) .
\]

In this expression, the coherence factors have cancelled with the quasi-particle density of states. Thus, in a BCS superconductor, the attenuation coefficient \( \alpha(T) \) should follow the law

\[
\alpha(T) \propto f(\Delta_0(T)) ,
\]

(10.224)
where \( f(x) \) is the Fermi function and \( \Delta_0(T) \) is the superconducting gap. Thus, for temperature far below \( T_c \), the attenuation coefficient should be thermally activated

\[
\alpha(T) \sim \exp \left[ -\beta \Delta_0 \right].
\]  

(10.225)

The above derivation emphasizes that, if \( q \) is defined as the polar axis, it is the electrons which have \( k \) vectors near the equatorial plane of the spherical Fermi surface that provide the dominant contribution to the attenuation of sound waves. Furthermore, since the contribution from this region of \( k \) space is weighted by a function depending on \( E_k/k_B T \), the presence of nodes of the order parameter within this equatorial plane may result in a power law temperature dependence of \( \alpha_q(T) \).

To illustrate the origin of the anisotropy, consider the clean limit of a polar–like superconductor with a line of nodes in the equatorial plane of the Fermi surface [411]. When the propagation vector \( q \) is aligned precisely along the polar axis \( \hat{d} \), the attenuation process primarily involves excitations on the line of nodes and, therefore, the attenuation coefficient resembles that of the normal state. However, if the direction of \( q \) is slightly rotated, the attenuation will only involve the low energy excitations near two isolated points on the line of nodes. Hence, one expects that the attenuation coefficient \( \alpha_q(T) \) will vary linearly with \( T \). The coefficient of the linear \( T \) term will depend sensitively on the angle \( \langle \hat{d}, \hat{q} \rangle \). For an ABM–like state, one may expect that if the \( q \) vector is oriented in a plane exactly perpendicular to the direction of \( \hat{d} \)

\[ ^{10} \text{For the ABM state } \hat{d} \text{ is in the direction of the polar axis.} \]
nodes. In this case, one expects that in this case, the attenuation coefficient should vary linearly with $T$. For other orientations the density of low energy excitations is reduced, so $\alpha_q(T)$ is expected to be proportional to $T^2$.

Most of the heavy–fermion superconducting materials are not in the clean limit, with the the exceptions of UPt$_3$ and CeCoIn$_5$. However, similar types of anisotropic results and pseudo–selection rules have been obtained for systems with resonant impurity scattering and high concentrations [157,412,413]. For example, in the dirty limit, the attenuation of transverse sound waves [414] is proportional to

$$\alpha_q(\omega) \propto \omega^2 \sum_{\hat{k}} \left( - \frac{\partial f}{\partial E_{\hat{k}}} \right)^2 \tau_{\hat{k}}(E) \left( \frac{\xi(\hat{k})}{E_{\hat{k}}} \right)^2 \left[ \hat{k} \cdot \hat{q} \right]^2 \left[ \hat{k} \cdot \hat{\epsilon} \right]^2,$$

(10.226)

where $\xi(\hat{k}) \equiv e(\hat{k}) - \mu$. For a superconductor with a line of nodes and at low temperatures, the largest contribution comes from $\hat{k}$ values close to the nodes. Due to the geometric factors, the attenuation is small if either the propagation vector $q$ or the polarization $\hat{\epsilon}$ is directed towards the nodes and is larger for other orientations. Hence, even in the dirty limit, the anisotropy can be used to determine the positions of the nodes in the superconductors order parameter.

In the heavy–fermion superconductors UBe$_{13}$ and UPt$_3$, the low temperature attenuation coefficients have power law temperature dependences, suggesting that the gaps are anisotropic and have nodes. The exponent of the power law temperature–dependence not only varies with the direction of propagation but also depends upon the polarization of the sound waves.

For the hexagonal compound UPt$_3$, Müller et al. [405] measured the attenuation coefficient for both longitudinal and transverse sound propagating...
along the c-axis. At temperatures sufficiently below $T_c$, the transverse [405] and longitudinal waves [27, 30] seemed to show a $T^2$ dependence of the attenuation rate. However, a fit to the attenuation of longitudinal sound over a wider temperature range, yields a $T^3$ dependence [405]. The attenuation of transverse sound waves propagating in the basal plane is dependent upon the direction of the polarization. Transverse sound waves propagating in the basal plane but with polarizations also in the basal plane, showed an attenuation which is linear in $T$ [406]. This is in direct contrast with the attenuation of transverse waves propagating in the basal plane, but with the polarization along the c-axis, which have an attenuation coefficient that shows a $T^2$ or $T^3$ [407] temperature dependence. Since the polarization dependence vanishes in the normal state, this is strong evidence that the anisotropy is a feature of the superconducting state. However, the nature of the order parameter is not easily discerned from these experiments. For a polar–like state with lines of nodes, the longitudinal attenuation should have a quasi–linear $T$ dependence or, for an ABM–like state with point nodes, the attenuation should vary as $T^2$ [157, 412]. The experimental observations of the longitudinal attenuation rate, therefore, favor an interpretation based on ABM–like states [411, 415] and rule–out polar–like states. However, the $T$ dependences found in the transverse sound wave experiments of Shivaram et al. [406] do not fit the predictions for ABM–like states with point nodes but instead fit the theoretical results for polar–like states with lines of nodes.

For UBe$_{13}$, measurements below 0.9 K [26] showed that the attenuation of longitudinal sound waves followed a $T^4$ variation which implies the existence of an ABM–like state with point nodes.

**Electromagnetic Response**

The electromagnetic absorption spectra of an $s$–wave superconductor has been calculated by Mattis and Bardeen [416], using the Kubo formulae. On assuming non–conservation of momentum, either caused by the presence of impurities or by the samples surface, the absorption spectrum is given by the integral

\[
\frac{\sigma_s}{\sigma_n} = \int_{-\infty}^{\infty} dE \rho_{BCS}(E) \rho_{BCS}(E - \hbar\omega) \left( \frac{f(E - \hbar\omega) - f(E)}{\hbar\omega} \right) \left( 1 + \frac{\Delta_0^2}{E(E - \hbar\omega)} \right)
\]

for $\hbar\omega > 2\Delta_0$. At $T = 0$, the absorption is evaluated in terms of the complete elliptical integral functions $E(x)$ and $K(x)$ as

\[
\frac{\sigma_s}{\sigma_n} = \left( 1 + \frac{2\Delta_0}{\hbar\omega} \right) E\left( \frac{\hbar\omega - 2\Delta_0}{\hbar\omega + 2\Delta_0} \right) - \left( \frac{4\Delta_0}{\hbar\omega} \right) K\left( \frac{\hbar\omega - 2\Delta_0}{\hbar\omega + 2\Delta_0} \right)
\]

for $\hbar\omega > 2\Delta_0$. At $T = 0$ where no thermally excited quasi–particles are present, the optical conductivity is zero for frequencies in the range
Fig. 10.63. The frequency dependence of the real part of the $T = 0$ optical conductivity calculated for various superconducting phases. The BCS phase conductivity exhibits a threshold at $\hbar \omega = 2 \Delta_0$. The ABM and polar phases have nodes in the order parameter, therefore, the respective conductivities should show power law variations at low frequencies.

$2 \Delta_0 > \hbar \omega > 0$. At higher frequencies, the incident photon can be absorbed through a process in which a Cooper pair is broken and two quasi-particles are created. Since the coherence factors are reduced near the gap edge, the a.c. conductivity shows a continuous increase above the threshold frequency and approaches the normal state conductivity at frequencies much greater than the gap frequency. Thus, as seen in Fig. 10.63, the area under the theoretically predicted curve $\sigma_s(\omega)$ is smaller than found in the normal state. The $\omega$ variation of $\sigma(\omega)$ calculated by Mattis and Bardeen is in agreement with experiments on In [417]. There is also good agreement between the theoretical and experimentally observed temperature dependence of $\sigma(\omega)$ for example, as found from measurements of the microwave surface impedance of Zn [418].

As shown by Tinkham and Ferrell [419], the inequality $\sigma_s(\omega) < \sigma_n(\omega)$, which is valid for all finite frequencies, has the consequence that the optical sum rule

$$\int_0^\infty d\omega \sigma(\omega) = \frac{\pi n e^2}{2m}$$

(10.229)

is not satisfied, if the integration is performed down to a finite cut off $\epsilon$ at the lower limit. Hence, the conductivity must have a zero frequency delta function spike in order to satisfy the optical sum rule. This spike represents the absorption of energy from d.c. electric fields which produce accelerated supercurrents. This spike is of special significance as causality connects the $\delta(\omega)$ contribution to the real part of the conductivity to a $1/\omega$ variation in the imaginary part of the conductivity. The existence of the $1/\omega$ term shows that supercurrent will flow in response to a uniform d.c. vector potential $A$. 

thereby screening the external magnetic field. The ensuing non–local relation is similar to the (local) London relation

$$ \overline{J}(r) = - \frac{c}{4 \pi \lambda_L^2} \overline{A}(r) $$

(10.230)

which involves the London penetration depth \( \lambda_L \). Within the BCS theory, the penetration depth \( \lambda(T) \) should have a leading exponential low temperature variation [420]. The calculated temperature dependence of the penetration depth is given by

$$ \frac{\lambda(T)}{\lambda(0)} - 1 \propto T^{-\frac{1}{2}} \exp \left[ - \frac{\Delta_0}{k_B T} \right], $$

(10.231)

since the Fermi surface is completely gapped in \( s \)-wave superconductors.

For anisotropic superconductors which have nodes in the order parameter, one expects very different results. First, since the angular average of the order parameter vanishes, and since the tensorial nature of the conductivity has been ignored, the coherence factors are reduced to unity. Hence, the expression analogous to that of Mattis and Bardeen for the dirty limit of the absorption spectrum is just given by the convolution of the quasi–particle density of states

$$ \sigma_s/\sigma_n = \int_0^{\hbar \omega} dE \rho_{qp}(E)\rho_{qp}(E - \hbar \omega) \left( \frac{f(E - \hbar \omega) - f(E)}{\hbar \omega} \right). $$

(10.232)

Secondly, due to the existence of nodes, the quasi–particle density of states is finite and, therefore, the conductivity is expected to be finite down to zero frequency. For an order parameter with point nodes, one expects that the above expression for the conductivity should vary as \( \omega^4 \) at low frequencies while for an order parameter with line nodes, one expects an \( \omega^2 \) variation. The electromagnetic absorption spectra for the BCS, ABM and polar states are shown in Fig. 10.63. For a more general description of electromagnetic absorption, incorporating the tensorial nature of the conductivity and the effects of impurity scattering, the interested reader is referred to the article of Hirschfeld et al. [421]. From an analysis of this type, Lee [394] found the surprising result that the \( \omega \to 0 \) limit of the conductivity has a value which is universal and independent of the impurity scattering rate. However, if the impurity scattering is sufficiently strong, Lee [394] has shown that the electronic states in the superconducting phase may be localized even though the electronic states in the normal state are not. The increased tendency for localization of the superconducting electrons is caused by the reduction of the effective dimension of the space in which the quasi–particles close to the nodes are free to move. The localization leads to the a.c. conductivity being dominated by the thermal activation of quasi–particle excitations across the mobility gap, despite any power law energy variation of the quasi–particle density of states near the Fermi energy.
The temperature dependence of the surface impedance of UBe$_{13}$ has been measured [422], and compared with theoretical predictions based on the BCS state. The value of $\Delta_0/k_B T_c$ was treated as an adjustable parameter. The experimentally determined surface reactance shows a coherence peak just below $T_c$, which is well reproduced by Mattis–Bardeen theory [416], and less well so by the theory of Skalski et al. [423] which incorporates the effect of a finite spin–flip scattering rate caused by magnetic impurities. However, a single value of $\Delta_0/k_B T_c$ does not fit the data at all frequencies, which indicates that the order parameter corresponds to $l \neq 0$. In fact, subsequently anomalous structure (shown in Fig. 10.64) was identified [424] in the surface resistance of UBe$_{13}$ below 0.8 $T_c$, which was attributed to collective excitations of an $l \neq 0$ superconducting order parameter.

Since, as seen in Fig. 10.63, the spectral weight below twice the maximal gap $2\Delta_0$ is diminished below the normal state conductivity, the zero–frequency delta function present in $\sigma_s(\omega)$ is also expected to exist in the anisotropic superconducting phases, albeit with reduced weight. On employing the Kramers–Kronig relations, one can infer that the penetration depth
should have a power law temperature dependence of the form

$$\frac{\lambda(T)}{\lambda(0)} - 1 \propto \left(\frac{T}{T_c}\right)^n,$$

where the exponent $n$ depends on the node structure of the superconducting order parameter. Power law temperature variations of the penetration depth have been observed in heavy–fermion superconductors for example, a $T^2$ power law dependence has been observed in UBe$_{13}$ [425]. By contrast, in UPt$_3$ the superfluid density measured by $\mu$SR experiments [426, 427] was also found to have a power law temperature dependence but one in which the exponent is anisotropic. Since the main contribution to the superfluid density is governed by the nodes in the superconducting order parameter, the magnetic field dependence of the penetration depth can be significant. Yip and Sauls [428] have suggested that this non–linear Meissner effect might be used to probe the momentum space positions of the nodes in the order parameter. However, Li et al. [429] find that in general, the non–local nature of the electromagnetic response does mask any non–linear Meissner effect, except under special circumstances.

**Tunnelling measurements**

Measurements of quasi–particle tunnelling at sufficiently low temperatures are expected to yield the quasi–particle density of states $\rho_{qp}(E)$. We assume that the tunnelling occurs between a normal metal with a relatively featureless density of state $\rho_N(E) \sim \rho(\mu)$ and a superconductor, and that the tunnelling matrix element $T$ is independent of $k$. If a bias voltage $V$ is applied across the junction, the tunnelling current $I$ is given by

$$I = \frac{2\pi}{h} e |T|^2 \int_{-\infty}^{\infty} dE \rho_N(E - eV) \rho_{qp}(E) \left[ f(E - eV) - f(E) \right].$$

The coherence factors do not enter the above expression [430], since the quasi–particle wave functions are reduced to the normal state wave functions in the barrier region. Hence, if the differential conductance $\sigma$ is defined by

$$\sigma = \frac{dI}{dV}$$

the differential tunnelling conductance is evaluated as

$$\sigma(V) = \frac{2\pi}{h} e^2 |T|^2 \rho(\mu) \int_{-\infty}^{\infty} dE \rho_{qp}(E) \left( -\frac{\partial f}{\partial E} \right) \bigg|_{E-eV}.$$  

At sufficiently low temperatures, the expression for the tunnelling conductance reduces to

$$\sigma(V) \propto \rho_{qp}(eV).$$
Hence, a measurement of the voltage dependence of the quasi–particle tunnelling conductance should yield the quasi–particle density of states [431]. Likewise, a similar analysis of quasi–particle tunnelling between two superconductors should yield the joint density of states with features at the sum and difference of the characteristic energies of the superconducting density of states for the two materials. For two $s$–wave superconductors at finite temperatures, a discontinuity occurs in the tunnelling current for a voltage $V_+$ corresponding to the sum of the two superconducting gaps, while a weak temperature dependent logarithmic singularity occurs in the current at the voltage $V_-$ corresponding to the difference of the gaps [431, 432]

\[
e V_+ = \Delta_1 + \Delta_2 ,
\]
\[
e V_- = | \Delta_1 - \Delta_2 | .
\]  

The observation of the quasi-particle density of states and, therefore, the characteristic van–Hove singularities and the low–energy variation, should provide information about the nature of the order parameter. However, it should be noted that the presence of the surface may locally distort the superconducting phase [433]. In this case, the tunnelling matrix elements may become orientational dependent and the local density of states may differ from the bulk quasi–particle density of states.

The best tunnelling measurements obtained to date are those on UPd$_2$Al$_3$. The junctions consisted of high quality UPd$_2$Al$_3$ films which were separated from the strong coupling superconductor Pb by a thin layer of Al [434]. A small magnetic field was applied in order to suppress the superconductivity of Pb. For temperatures below the superconducting transition of UPd$_2$Al$_3$, the tunnelling conductance developed a minimum at zero bias voltages and a large peak structure at a voltage of the order of 0.24 mV. The large peak structure resembles the van Hove singularities often found in superconducting quasi–particle density of states at $\Delta_0$ (see Figs. 10.23 and 10.24). On identifying this voltage with the gap energy, one finds that the universal ratio $\Delta_0(0)/k_B T$ is of the order of 3.71 [435]. The differential conductance also showed a fainter peak at a voltage of 1.25 mV, which was attributed to strong coupling corrections. These features in the density of states are assumed to originate from coupling to unusual antiferromagnetic spin excitations seen in inelastic neutron scattering experiments [350, 436]. By contrast, the interpretation of tunnelling experiments on CeCu$_2$Si$_2$ is not so clear cut. The tunnel junctions were constructed from CeCu$_2$Si$_2$ which were separated by a thin oxide layer from an overlayer of Pb. The measurements showed that, for temperatures below the $T_c$ of CeCu$_2$Si$_2$, the tunnelling conductance resembles the superconducting density of states of Pb but is superimposed with very small features that were attributed to a gapless superconducting quasi–particle density of states of CeCu$_2$Si$_2$ [437].

**Point Contact Spectroscopy**

The difficulty of fabricating good tunnel junctions and the small tunnelling
probabilities associated with oxide layers has hampered tunnelling experiments. On the other hand, measurements of the differential conductance of point–contacts between a superconductor and metal are expected to produce larger currents. In this case, the Cooper pair wave function of the superconductor extends into the metal and Andreev reflection may occur [438] along with the usual single–particle transfer process. That is, an electron of momentum $\mathbf{k}$ incident on the boundary between the metal and superconductor may combine with a normal state electron of momentum $-\mathbf{k}$ to form a Cooper pair that subsequently resides within the superconducting condensate. This process can be viewed as an incident electron, with energy $E < \Delta_0$, inside the metal being scattered from the surface of the superconductor and emerging in the metal as a reflected hole, thereby transferring a net charge of $2\,e$ across the junction. The role of Andreev reflection in point contact spectroscopy on conventional $s$–wave superconductors was pointed out by Blonder et al. [439]. Since the conductance depends on an interface potential which in part models the decay of the pairing potential in the normal metal, the conductance smoothly evolves between the result for classic tunnelling expressed by Eqn. (10.236) and the extreme Andreev limit. In the extreme Andreev limit, the conductance of an $s$–wave superconductor – metal contact shows a zero bias peak which is twice as great as the normal state conductance of the junction. The magnitude of the peak height of the normalized conductance is two since a charge of $2\,e$ is transferred across the junction for each normal–metal electron with energy $E < \Delta_0$ that falls incident on the surface. The conductance recovers to the normal state value at higher voltages ($e\,V > \Delta_0$) as other electron transfer processes gradually take over. Bruder extended the analysis of Andreev reflection to the case of unconventional superconductors [440] and found that the energy of the peak is extremely dependent on the type of superconducting order parameter and the direction of the incident electron’s momentum. In the usual geometry of point contact measurement, the electrons have varying angles of incidence with the boundary and, therefore, conductance measurements yield weighted orientational averages of functions of the order parameter.

Early Point contact tunnelling measurements were made on UPt$_3$ and UBe$_{13}$ and various metals [441, 442] but did not lead to reliable estimates of the gaps for the heavy–fermion superconductors. Later, measurements on UPt$_3$ [443–445] showed that distinct minima in the differential conductance – voltage relation occur for current flow along the $c$–axis but are generally absent for current flow in the basal plane. The differential conductance shows significant variation with the surface treatment. These results indicate that the superconducting order parameter has an anisotropic dependence on $\mathbf{k}$. The amplitude of the zero bias peak, when normalized to the conductance at large voltages, is an order of magnitude smaller than expected from theory. A similar discrepancy with the theoretical magnitude of the peak was found in URu$_2$Si$_2$ [446]. On defining the strength of the zero bias conductance
peak as the area between $\sigma(V)$ in the superconductor and the normal state background, the strength vanished close to $T_{c2}$. The vanishing of the strength between $T_{c1}$ and $T_{c2}$ is very surface sensitive but indicates that Andreev reflection is suppressed in the A phase. A similar reduction of the strength was found when a magnetic field was applied in the basal plane.

Point contact measurements on URu$_2$Si$_2$ [446] are of particular interest since they showed a gap with magnitude of approximately 10 meV opened up in the conductance spectrum near the transition temperature of 17.5 K. As also observed in point contact measurements in UPt$_3$ [444], the shape of the zero bias conduction peak for URu$_2$Si$_2$ is consistent with an order parameter that has lines of nodes [446].

In contrast to the very small magnitude of the zero bias conductance peak found in UPt$_3$ and URu$_2$Si$_2$, the magnitude of the conductance peak in UBe$_{13}$ [447] is roughly a factor of 5 times larger than the theoretical value for an $s$-wave superconductor. The enhancement of the zero bias anomaly was attributed to the formation of an Andreev surface state, which can occur if there is a non–trivial dependence on the angle subtended by the nodes of the order parameter to the normal to the interface [448]. As the bias voltage was increased, the zero bias conductance peak of UBe$_{13}$ was followed by a minimum which was reduced from the normal state value and then showed a sharp increase as it recovered to the normal state value. The variation of the differential conductivity with voltage is shown in Fig. 10.65. The sharp increase occurred at a temperature–dependent voltage which was of the order of magnitude 0.25 mV at 330 mK. Such sharp changes of the conductance have not been observed for $s$–wave superconductors but have been predicted to occur at the gap voltage $eV = \Delta_0$ for junctions with anisotropic superconductors [448]. If the temperature dependent characteristic voltage is interpreted as being the magnitude of the order parameter $\Delta_0(T)$, then UBe$_{13}$ would correspond to a universal ratio $2\Delta_0(0)/k_B T_c$ of about 6.7 which is far greater than the BCS value of 3.5, and is also greater than the ratio predicted for most $p$–wave phases (ABM 4.6, polar 4.9) but is more comparable with the value of 6.2 predicted for the $m = 0$ $d$–wave phase.

**Josephson Tunnelling**

Josephson tunnelling involves the tunnelling of Cooper pairs between two superconductors [449]. A d.c. tunnel current may appear even in the absence of an applied voltage but also appears as an a.c. current if a voltage is applied. The a.c. current is expressed in terms of the phase difference between the wave functions of the two superconductors

$$I(t) = I_0 \sin \left( \frac{2eV t}{\hbar} + \Delta \varphi \right). \quad (10.239)$$

The phase difference not only has contributions from the intrinsic phases of the superconductors but also has contributions from any magnetic vector potential that may be present at the junction. When integrated over the finite size of the contact, this term can give rise to a Fraenhofer diffraction
Fig. 10.65. The differential conductivity of a UBe$_{13}$-Au point contact at $T = 330$ mK, as a function of voltage. The height of the zero–bias anomaly is roughly five times greater than is expected for an $s$–wave superconductor. The solid line shows an estimate of the Kondo contribution to $G(V)$. [After Wälti et al. (2000), [447]]

pattern [450]. The leading order contribution to the Josephson coupling can be calculated using second order perturbation theory [449]. To lowest order there should be no Josephson current between a singlet and triplet superconductor [451], since spin is conserved in the tunnelling process. However, even in this case, spin–orbit interaction and higher order processes may produce a non–zero Josephson current. If the tunnelling is due to a fourth order process, the Josephson frequency is expected to be given by $4\,eV/\hbar$. Since the presence of the surface locally violates certain rotational symmetries contained in the point group, it is possible for relatively large Josephson currents to flow between superconductors with different orbital symmetries. In fact, the magnitude of the order parameter at the surface may even vary with the relative orientation of the boundary and the node directions. Due to this, it is possible to extract the symmetry of the order parameter from Josephson tunnelling measurements [452]. However, the Josephson effect is a very weak effect and sensitive to impurities and inhomogeneities, since the total coupling energy for a conventional Josephson junction is estimated to be only of the order of 1 eV. For the heavy–fermion systems, the preparation and characterization of good surfaces and junctions represent formidable experimental problems. Therefore, there has been only limited progress in the investigation of the Josephson effect in heavy–fermion superconductors.

A d.c. Josephson current was found to exist between CeCu$_2$Si$_2$ and Al [441]. The Josephson current vanished at the $T_c$ of CeCu$_2$Si$_2$ with applied magnetic fields greater than the upper critical field of Al but smaller than the critical field of CeCu$_2$Si$_2$. Hence, the tunnelling current involved the superconducting phases of both materials. The application of magnetic fields
produced irregular Fraunhofer diffraction patterns which were smeared out. The smearing was attributed to the irregular geometry of the junctions. As the observed value of the critical current was quite large, having a maximum magnitude that is 80% of the BCS value, it appears as if the Josephson coupling is of second order \[453\] and not of fourth order. Furthermore, since Al is known to be a singlet superconductor, the large coupling strength indicates that CeCu$_2$Si$_2$ is also a singlet superconductor.

No Josephson currents were found to flow across weak links between UPt$_3$ surfaces \[441\]. However, a Josephson current, with an irregular Fraunhofer pattern and well defined Shapiro steps was observed between UPt$_3$ and Nb in a superconductor – normal metal – superconductor junction \[454\]. The critical current measured for junctions where the current flow is primarily along the c–axis of the UPt$_3$ single crystal is significantly larger than for junctions where the current flows along the basal plane. The critical current temperature relations show clear kinks at the lower critical temperature $T_{c2}$. For temperatures below $T_{c2}$, the slope of the critical current – temperature relation is large for current flow along the c–direction, and smaller for current flow in the basal plane. For temperatures above $T_{c2}$, the slope of the critical current temperature relation for flow in the basal plane changes to a larger value but the curve representing flow along the c–axis is rather flat. The change in the anisotropy at $T_{c2}$ seems to indicate that the anisotropy in the current flow is related to the unconventional nature of the superconductivity in UPt$_3$. It should be noted that, since the anisotropy measurements were made on junctions with different surfaces, the apparent anisotropy possibly could reflect a difference in the properties of the interfaces. A much larger anisotropy was inferred from measurements of Josephson currents through point contacts between URu$_2$Si$_2$ and Nb \[455\] where no current was observed for contacts aligned parallel to the c–axis but finite currents were found for contacts aligned parallel to the a–b directions. The absence of Josephson currents flowing along the c–axis could, however, have many other possible causes.

No Josephson tunnelling currents were observed to flow across a weak link between two surfaces of UBe$_{13}$. In a junction between Al and UBe$_{13}$, superconductivity was introduced in UBe$_{13}$ by the proximity effect for temperatures below the superconducting transition of Al but above the superconducting transition for UBe$_{13}$. In this temperature regime, a weak Josephson current was observed between these materials. A proximity induced Josephson current was also found to occur across a point contact between UBe$_{13}$ and Ta at temperatures below $T_c$ for Ta and above $T_c$ for UBe$_{13}$. This Josephson current was destroyed as the temperature was lowered below the $T_c$ of UBe$_{13}$ \[456, 457\]. This was taken as evidence that the superconducting order parameter of UBe$_{13}$ competes with the superconductivity of Ta and hence, are of different symmetry. The analysis presented in Ref. \[457\] suggested that the Cooper pairs were spin–triplet, however, spin–singlet $d$–wave pairing would
be more consistent with the experimental observations. In particular, when illuminated with microwave radiation of frequency $\omega$, the current d.c. voltage relation exhibited Shapiro steps of magnitude $\Delta V = \hbar \omega / 2e$, instead of $\Delta V = \hbar \omega / 4e$ as would be expected for a fourth order Josephson coupling between singlet and triplet superconductors [451,458]. The interpretation of these experiments is enigmatic since a conventional Josephson tunnelling current, with an irregular Fraenhofer pattern (see Figs. 10.66 and 10.67) and conventional Shapiro steps (shown in Fig. 10.68), was observed at temperatures below 0.94 K between UBe$_{13}$ and Nb in a fairly well defined superconductor – normal metal – superconductor geometry [459]. The Shapiro steps were observed to have a magnitude of $\Delta V = \hbar \omega / 2e$, as expected for a second order Josephson coupling between two singlet superconductors. On the other hand, the magnitudes of the critical currents were remarkably small, being two orders of magnitude smaller than the critical currents observed in UPt$_3$. However, as the critical currents were limited by heating, it was not possible to determine whether the magnitude of the Josephson coupling in UBe$_{13}$ was consistent with the tunnelling being due to a fourth order process or a second order process.
Fig. 10.67. The temperature dependence of the critical Josephson current $J_c$ and the junction resistance $R$, near $T_c$ for a UBe$_{13}$-Nb junction. After Shibata et al. (1999), [459]

Fig. 10.68. The $I(V)$ relation for a UBe$_{13}$-Nb junction, showing conventional Shapiro steps when an ac current of frequency 100 kHz is superimposed on the dc current. [After Shibata et al. (1999), [459]]

10.4.3 Dynamic Magnetic Properties

Nuclear Magnetic Resonance

As previously mentioned, nuclear magnetic resonance experiments yield several important quantities: the Knight shift and the nuclear spin relaxation rates which are $1/T_1$ the longitudinal relaxation rate, and the transverse relaxation rate $1/T_2$. The changes in behavior of these quantities on entering
the superconducting phase does give information about the nature of the density of magnetic excitations in the superconductor.

**The Knight shift**

The Knight shift has many contributions, one important contribution provides a measure of the local part of the static susceptibility of the itinerant electrons which produces a magnetic polarization at the nuclear site. For heavy–fermion superconductors, the normal state Knight shift is expected to be dominated by the enhanced Pauli spin susceptibility, though spin–orbit coupling will introduce an orbital part. However, in the superconducting state, the Knight shift is expected to be dominated by the diamagnetic susceptibility produced by the supercurrent shielding the external field. The Pauli spin susceptibility will be modified by the superconductivity, and provide information about the pairing. The zero field susceptibility is defined as a derivative of the magnetization $\chi(T) = (\frac{\partial M}{\partial H})$. The magnetization that is produced by the electronic spins aligning with a magnetic field applied along the $z$–axis is given by

$$M_z = \left(\frac{g \mu B}{2}\right) \sum_k \left[ f(E_{\uparrow,k}) - f(E_{\downarrow,k}) \right]$$  \hspace{1cm} (10.240)

which is expressed in terms of the Fermi–distribution for quasi–particles with spin $\sigma$ and quasi–particle energy $E_{\sigma,k}$. The field dependence of the quasi–particle energies depends on the type of spin pairing, so we shall discuss the different types of spin pairings separately.

**Singlet Pairing**

For singlet pairing, the magnetic field couples to the spins of the quasi–particles via the Zeeman energies. As can be seen from inspection of the matrix in Eqn. (10.58), only the time reversal partners pair when $\vec{d}(k) \equiv 0$. The quasi–particles consist of broken pairs, i.e., electrons of spin $\sigma$ and holes of spin $-\sigma$. Since a down–spin hole has the same Zeeman energy as an up–spin electron, the quasi–particle energies depend on the magnetic field through

$$E_{\sigma,k} = E_{H=0,k} - \left(\frac{g \mu B \sigma H}{2}\right)$$  \hspace{1cm} (10.241)

and so the spin susceptibility takes the usual form

$$\chi_{S=0}(T) = 4 \left(\frac{g \mu_B}{2}\right)^2 \int_0^\infty dE \rho_{S=0}(E) \left(-\frac{\partial f}{\partial E}\right).$$  \hspace{1cm} (10.242)

The BCS density of states should be used in the above expression, for an $s$–wave superconductor. In this case, the susceptibility tends to zero as $T \to 0$ in an exponentially activated way $\chi_{BCS}(T) \sim \exp[-\Delta_0/k_B T]$. The exponential vanishing of the spin susceptibility occurs as the electrons form singlet
Susceptibilities of Singlet Superconductors

Fig. 10.69. The calculated spin susceptibilities of singlet superconducting phases. The susceptibilities are normalized to the normal state susceptibility. The susceptibilities in the singlet superconducting phases all vanish as \( T \to 0 \). The susceptibility of the BCS phase is given by the Yosida function, which vanishes exponentially at low temperatures. The susceptibilities of the isotropic and \( m = 1 \) \( d \)-wave phases vary as powers of the temperature, at low temperatures.

Pairs in the ground state, and the finite spin moment is caused by thermal population of quasi-particles [460]. For a singlet superconductor that has point nodes, the density of states varies as \( E^2 \) at low energies and, therefore, one expects that \( \chi_{S=0}(T) \propto T^2 \) for \( T \ll T_c \). Whereas for a singlet superconductor which has line nodes, the density of states is given by \( \rho_{S=0}(E) \propto E \) at low energies, hence one obtains \( \chi_{S=0}(T) \propto T \). The temperature dependence of the calculated spin susceptibility expected for various singlet spin superconducting phases is shown in Fig. 10.69.

Thus, in the spin singlet phases, the spin susceptibility could be expected to vanish as \( T \to 0 \). However, spin–orbit coupling will produce a residual susceptibility that depends on the ratio of the superconducting coherence length, \( \xi_0 \), to the mean free path due to spin–orbit scattering, \( l_s \). In the presence of spin–orbit coupling, the spin is no longer a good quantum number for the single–particle eigenstates and the spin–up and spin–down states are mixed. In the limit that the strength of the spin–orbit coupling \( \lambda \to L \to S \) is so large that \( \lambda \gg \Delta_0 \), the average value of \( \sigma_z \) for a single particle state tends to zero. The spin susceptibility is, therefore, reduced. From the Kramers–Kronig relations, one observes that a significant contribution to the normal state
\( \chi(T) \) comes from single–particle states with excitation energies of the order of the spin–orbit scattering rate \( \hbar/\tau_{so} \) which is, by assumption, greater than \( \Delta_0 \). As an opening up of a superconducting gap at the Fermi energy is not expected to change the contribution of these higher energy states, one finds that the susceptibility in the superconducting state can remain comparable in magnitude to the normal state value. According to Anderson [461, 462], the normalized susceptibility should have the two limits. The limit of strong spin–orbit scattering is defined by \( l_{so} \ll \pi \xi_0 \), where \( \xi_0 = \hbar v_F/\pi \Delta_0 \) and \( l_{so} = v_F/\tau_{so} \), and the limit of weak spin–orbit scattering is defined by \( l_{so} \gg \pi \xi_0 \). In the limit of strong spin–orbit scattering, the normalized susceptibility is given by [463]

\[
\frac{\chi_{BCS}(0)}{\chi_n} \approx 1 - \frac{8}{3 \pi} \frac{l_{so}}{\xi_0}.
\]  

For weak spin–orbit scattering, the susceptibility ratio is given by

\[
\frac{\chi_{BCS}(0)}{\chi_n} \approx \frac{3 \pi}{8} \frac{\xi_0}{l_{so}}.
\]

Hence, the existence of a partial Meissner effect at \( T = 0 \) does not necessarily imply the presence of either triplet or gapless superconducting phases.

**Triplet Pairing**

For triplet pairing, the above argument indicates that a finite susceptibility could be expected to arise due to the \( S = 1 \) spin of the Cooper pairs. The way the susceptibility depends on the orientation of the field \( \vec{H} \) relative to the direction of \( \vec{d} \), for a direction of \( \vec{d} \) independent of \( k \), is described below.

First, if \( \vec{d} \) is parallel to \( \vec{H} \) for all \( k \), then, as \( \vec{H} \) is the direction of quantization of \( \sigma \), \( \vec{d} \) is parallel to \( \hat{z} \) and so \( S_z = 0 \). Since \( d_{S_z=0} \) is the only finite component of the order parameter, the off–diagonal blocks in the mean–field Hamiltonian Eqn. (10.58) are proportional to \( \sigma_x \). And so, as in the singlet case, only the same time reversal partner states are coupled. Thus, one obtains the same Zeeman type of coupling as the singlet case, \( E_{\sigma,k} = E_{H=0,k} - \frac{i}{2} (g \mu_B \sigma \vec{H} \cdot \vec{d}) \), and the susceptibility is given by the same expression as Eqn. (10.242) but with the appropriate triplet density of states.

\[
\chi_{S=1,\parallel}(T) = 2 \left( \frac{g \mu_B}{2} \right)^2 \sum_k \left( -\frac{\partial f}{\partial E_k} \right) = 4 \left( \frac{g \mu_B}{2} \right)^2 \int_0^{\infty} dE \rho_{S=1}(E) \left( -\frac{\partial f}{\partial E} \right).
\]

Hence, the spin susceptibility has a linear \( T \) variation for a density of states with lines of nodes or a \( T^2 \) variation with point nodes.

Secondly, if \( \vec{H} \) is perpendicular to \( \vec{d} \) for all \( k \), then, as \( \vec{d} \) is perpendicular to \( \hat{z} \), the pairs are in a linear combination of states with \( S_z = \pm 1 \). The
off–diagonal blocks of the mean–field Hamiltonian are of diagonal form and only couple electrons and holes with the same spin directions. Then, the quasi–particle energies are given by

\[ E_{\sigma,k}^2 = \left[ e(k) - \mu - \left( \frac{g \mu_B \sigma H}{2} \right) \right]^2 + \left| d_x(k) + i \sigma d_y(k) \right|^2. \] (10.246)

Furthermore, since

\[ \left( \frac{\partial E_{\sigma,k}}{\partial H} \right) = - \left( \frac{g \mu_B \sigma}{2} \right) \left( \frac{\partial E_{\sigma,k}}{\partial e_{\sigma}} \right), \] (10.247)

the expression for \( \chi_{S=1, \perp}(T) \) has the form

\[ \chi_{S=1, \perp}(T) = \sum_\sigma \left( \frac{g \mu_B \sigma}{2} \right)^2 \rho(\mu) \int_{-\infty}^{+\infty} de \left( \frac{\partial E_{\sigma}}{\partial e} \right) \left( - \frac{\partial f(E_{\sigma})}{\partial E_{\sigma}} \right) \]

\[ = 2 \left( \frac{g \mu_B}{2} \right)^2 \rho(\mu). \] (10.248)

Hence, in this case, the uniform static spin susceptibility retains the normal state value. In general, for triplet pairing, the orientational average of \( \chi_{S=1}(T) \) will have a magnitude of 2/3 the normal state susceptibility.

The sum of the quasi–particle energies are lowered when \( \vec{H} \) is perpendicular to \( \vec{d}(k) \). For an isotropic system like \(^3\)He, and a pairing vector which has a direction independent of \( k \) such as in the ABM phase, the vector \( \vec{d} \) will rotate to remain perpendicular to the field and the susceptibility will remain constant. On the other hand, heavy–fermion systems are expected to have strong spin–orbit coupling and crystalline anisotropy, therefore, the direction of \( \vec{d} \) is expected to remain constant when \( \vec{H} \) is applied. If the material has an anisotropy such that spins have an easy axis or plane, then \( \chi_{S=1} \) for that phase will be reduced if \( \vec{H} \) tilts away from the axis or plane. In such cases of strong anisotropy, the susceptibility tensor is given by the directional average

\[ \chi^{i,j}_{S=1}(T) =

2 \left( \frac{g \mu_B}{2} \right)^2 \sum_k \left( - \frac{\partial f}{\partial E_k} \right) \left[ \frac{d_i^*(k)d_j(k)}{d^*(k)d(k)} + \left( \frac{\partial E_k}{\partial e_k} \right) \delta_{i,j} - \frac{d_i^*(k)d_j(k)}{d^*(k)d(k)} \right] \] (10.249)

In the BW phase the zero temperature susceptibility is 2/3 of the normal state value, this occurs as the \( k \) averaged value of \( d^2 \) has one component parallel to \( \vec{H} \) which is suppressed, the other two components retain their normal values. The calculated spin susceptibilities expected for various triplet superconducting phases is shown in Fig. 10.70. The above discussion indicates
Fig. 10.70. The calculated spin susceptibilities of triplet superconducting phases. The susceptibility for the BW phase is isotropic. The susceptibilities of the ABM and polar phases are anisotropic, if the order parameter is pinned by the lattice. The susceptibilities vanish at low temperatures for applied fields which are parallel to the Cooper pair spin but remain unaffected for fields oriented perpendicular to the spin.

that, if the behavior of the hyperfine field is known (perhaps extrapolated from the normal state), the temperature dependence of the Knight shift in the superconducting state can yield information about the nature of the pairing.

In pure UBe$_{13}$, the muon Knight shift [322] exhibits a large reduction below $T_c$ with a magnitude similar to that found in weak coupling $s$–wave superconductors. The Knight shifts found for Th [322] and B doped samples [464] show no appreciable changes on entering the superconducting states which is consistent with the formation of spin–singlet Cooper pairs but with strong spin–orbit scattering or gapless phases caused by impurity scattering. The anisotropic Knight shift observed in CeCu$_2$Si$_2$ [465, 466] undergoes a significant reduction in the superconducting state, similar to the behavior observed in UBe$_{13}$. The reduction found in CeCu$_2$Si$_2$ is consistent with the vanishing of the spin susceptibility at zero temperature, as expected for a spin–singlet superconducting phase. In CeCoIn$_5$ [61], the decrease of the $^{59}$Co Knight shift in the superconducting state is large for fields along the $c$–axis and is hardly noticeable for fields in the perpendicular directions. However, the lack of any decrease in the perpendicular directions was attributed to a large temperature independent contribution to the susceptibility from the Co
Fig. 10.71. Temperature dependence of the muon Knight shifts in UPd$_2$Al$_3$, for fields applied parallel and perpendicular to the $c$ axis. [After Feyerherm et al. (1994), [469]]

Fig. 10.72. The calculated temperature dependence of the spin-lattice relaxation rate $1/T_1$ for the BCS, BW, ABM and polar phases. The rates are normalized to the normal state relaxation rate at $T_c$. A Hebel–Slichter peak occurs below $T_c$ for the BCS and BW phases, but is absent for the ABM and polar phases.
Fig. 10.73. The temperature dependence of the $^{9}$Be nuclear spin relaxation rate $1/T_1$ in $U_{1-x}Th_xBe_{13}$, for $x = 0$ and $x = 0.033$. The solid line is a fit to a $T^3$ power law below $T_c$, and the dashed line is the normal state Korringa law. [After MacLaughlin et al (12984), [25]]

3d orbitals. The observation of a smaller but isotropic decrease in the Knight shift of $^{115}$In below $T_c$ is supportive of a superconducting state which involves spin–singlet Cooper pairs.

The Knight shift has been measured in the superconducting state of single crystals of $UPt_3$ [467, 468]. For large fields [467], no appreciable change was observed on entering the superconducting phase for all directions of the applied field. However, a later study [468] showed a very small decrease occurred for fields aligned along either the b–axis or c–axis but only for fields such that $H_a < 5$ kOe and $H_c < 2$ kOe. This was interpreted as showing evidence for spin–triplet pairing, in which the superconducting vector order parameter is pinned to the lattice for small applied fields but for sufficiently large fields is free to rotate so as to follow the direction of the applied field.
This explanation rests on the unjustified assumption of very weak spin–orbit coupling in UPt$_3$ and also does not explain the extremely small magnitude of the change of Knight shift that occurs when the order parameter is pinned. However, since the crystals were of very high quality, the absence of a reduction of the spin susceptibility at low temperatures is not attributable to spin–orbit or to impurity scattering in a spin–singlet superconducting phase.

Although the normal state susceptibility and the $\mu$SR Knight shift of UPd$_2$Al$_3$ are anisotropic, the small and anisotropic change in the Knight shift which occurs below $T_c$ has been taken as evidence that the electrons form spin–singlet Cooper pairs. An analysis of the normal state data indicates that part of the anisotropy originates in the coupling. The dipole contribution is estimated to be three times stronger than the hyperfine field coupling. Although a small anisotropic change in the Knight shift is observed as the temperature is decreased below $T_c$, the analysis attributes the change to an isotropic reduction of the $f$ spin susceptibility [469]. The reduction has a magnitude of 11% which is only compatible with spin–singlet pairing of the quasi–particles if one partitions the $f$ susceptibility into separate quasi–particle and local moment contributions. This is in direct contrast with conclusions from Al NMR Knight shift studies of the isostructural compound UNi$_2$Al$_3$. The Knight shift measurements of UNi$_2$Al$_3$ have been interpreted as indicating that the quasi–particles form triplet–spin Cooper pairs [470]. Since the crystals are not axially symmetric, the crystals contain two inequivalent Al sites. As a consequence, the experiments on UNi$_2$Al$_3$ show two distinct NMR peaks for magnetic fields applied parallel to the $a$–axis. In UNi$_2$Al$_3$, the Knight shift predominantly comes from the hyperfine coupling which has a similar magnitude to that found in UPd$_2$Al$_3$. However, on reducing $T$ below $T_c$, the Knight shift observed for one peak did not show a change comparable to that found in UPd$_2$Al$_3$ and hence, it is argued that these measurements provide evidence for triplet–spin superconductivity. Due to the much larger $1/T_1$ contribution to the peak width for fields along the $c$–axis, these experiments were unable to determine if the Knight shift exhibits the full anisotropic Meissner behavior expected from a spin–triplet superconductor.

**Longitudinal Nuclear Spin Relaxation**

The temperature variation of the Spin Lattice relaxation rate $1/T_1$ can be drastically changed at the onset of superconductivity. This occurs as a result of the change in the quasi–particle excitation spectrum but also is due to a modification of the matrix elements for the coupling of the quasi–particle excitations to the nuclear spins. As the modification of the matrix elements of the coupling interaction, known as the coherence factor, involves the gap function, $1/T_1$ could provide additional information about the symmetry of the superconducting phase. The relaxation rate for a spin distribution aligned along the $z$ axis is driven by spin–flip fluctuations, and is given by the ex-
pression

\[ \frac{1}{T_1} = k_B T \left( g \mu_B \right)^2 \frac{1}{N} \sum_\mathbf{q} A(\mathbf{q})^2 \left[ \frac{\text{Im} \chi^{+,-}(\mathbf{q}; \omega_N)}{\hbar \omega_N} \right], \]  

where \( \omega_N \) is the nuclear Larmor frequency, and \( A(\mathbf{q}) \) is the averaged strength of the local hyperfine field. The factor \( \text{Im} \chi^{+,-}(\mathbf{q}; \omega) \) represents the density of states for magnetic spin–flip fluctuations. A typical value of the nuclear Larmor frequency is \( \hbar \omega_N \sim 10^{-7} \) meV and so, for all but in systems with exceptionally slow spin–fluctuations, one may approximate \( \omega_N \) by \( \omega_N = 0 \). This approximation could be expected to fail near a quantum critical point.

Just to illustrate the nature of the coupling to the superconductivity, we shall replace the full susceptibility by the lowest order polarization part or quasi–particle susceptibility.

The first step in evaluating the imaginary part of the susceptibility is to express the spin–flip operators in terms of the four component fields \( \Psi(\mathbf{k}) \), so the spin raising operator \( \hat{\sigma}^+(\mathbf{q}) \) is given by

\[ \hat{\sigma}^+(\mathbf{q}) = \Psi^\dagger(-\mathbf{k} - \mathbf{q}) \begin{pmatrix} \sigma^+ & 0 \\ 0 & -\sigma^- \end{pmatrix} \Psi(-\mathbf{k}), \]  

where \( \sigma^+ \) and \( \sigma^- \) are the \( 2 \times 2 \) Pauli spin matrices. The spin lowering operator \( \hat{\sigma}^-(\mathbf{q}) \) is given by

\[ \hat{\sigma}^-(\mathbf{q}) = \Psi^\dagger(-\mathbf{k} - \mathbf{q}) \begin{pmatrix} \sigma^- & 0 \\ 0 & -\sigma^+ \end{pmatrix} \Psi(-\mathbf{k}). \]  

In general, the matrix \( \hat{\sigma}^i \) corresponding to a spin operator \( \hat{\sigma}^i \) is a \( 2 \times 2 \) block diagonal matrix with the upper and lower diagonal elements given, respectively, by \( \sigma^i \) and \( (i \sigma_y) \sigma_i (-i \sigma_y) \), where the lower diagonal element reflects the effect of time reversal on the spins. The lowest order contribution to the susceptibility tensor \( \chi^{\alpha,\beta}(\mathbf{q}; \omega) \) is expressed in terms of the Fourier transform of the imaginary time single–particle Green’s functions. These Green’s functions are defined in terms of the Wick’s time ordered product of two four–component fields

\[ G(\mathbf{k}; \tau) = -< | \hat{T} \Psi(\mathbf{k}, \tau) \Psi^\dagger(\mathbf{k}, 0) | >. \]  

The susceptibility tensor can be written as the analytic continuation onto the real frequency axis of the trace

\[ \chi^{\alpha,\beta}(\mathbf{q}; \nu_m) = \]  

\[ k_B T \left( g \mu_B \right)^2 \frac{1}{N} \sum_{n,k} \frac{1}{2} \text{Trace}G(\mathbf{k} + \mathbf{q}; i \hbar (\omega_n + \nu_m)) \hat{\sigma}^\beta G(\mathbf{k}; i \hbar \omega_m) \hat{\sigma}^\alpha, \]  

where \( \omega_n \) is the nuclear Larmor frequency, and \( A(\mathbf{q}) \) is the averaged strength of the local hyperfine field. The factor \( \text{Im} \chi^{+,-}(\mathbf{q}; \omega) \) represents the density of states for magnetic spin–flip fluctuations. A typical value of the nuclear Larmor frequency is \( \hbar \omega_N \sim 10^{-7} \) meV and so, for all but in systems with exceptionally slow spin–fluctuations, one may approximate \( \omega_N \) by \( \omega_N = 0 \). This approximation could be expected to fail near a quantum critical point.

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where \( \omega_n \) is the nuclear Larmor frequency, and \( A(\mathbf{q}) \) is the averaged strength of the local hyperfine field. The factor \( \text{Im} \chi^{+,-}(\mathbf{q}; \omega) \) represents the density of states for magnetic spin–flip fluctuations. A typical value of the nuclear Larmor frequency is \( \hbar \omega_N \sim 10^{-7} \) meV and so, for all but in systems with exceptionally slow spin–fluctuations, one may approximate \( \omega_N \) by \( \omega_N = 0 \). This approximation could be expected to fail near a quantum critical point.

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where \( \sigma^+ \) and \( \sigma^- \) are the \( 2 \times 2 \) Pauli spin matrices. The spin lowering operator \( \hat{\sigma}^-(\mathbf{q}) \) is given by

\[ \hat{\sigma}^-(\mathbf{q}) = \Psi^\dagger(-\mathbf{k} - \mathbf{q}) \begin{pmatrix} \sigma^- & 0 \\ 0 & -\sigma^+ \end{pmatrix} \Psi(-\mathbf{k}). \]  

In general, the matrix \( \hat{\sigma}^i \) corresponding to a spin operator \( \hat{\sigma}^i \) is a \( 2 \times 2 \) block diagonal matrix with the upper and lower diagonal elements given, respectively, by \( \sigma^i \) and \( (i \sigma_y) \sigma_i (-i \sigma_y) \), where the lower diagonal element reflects the effect of time reversal on the spins. The lowest order contribution to the susceptibility tensor \( \chi^{\alpha,\beta}(\mathbf{q}; \omega) \) is expressed in terms of the Fourier transform of the imaginary time single–particle Green’s functions. These Green’s functions are defined in terms of the Wick’s time ordered product of two four–component fields

\[ G(\mathbf{k}; \tau) = -< | \hat{T} \Psi(\mathbf{k}, \tau) \Psi^\dagger(\mathbf{k}, 0) | >. \]  

The susceptibility tensor can be written as the analytic continuation onto the real frequency axis of the trace

\[ \chi^{\alpha,\beta}(\mathbf{q}; \nu_m) = \]  

\[ k_B T \left( g \mu_B \right)^2 \frac{1}{N} \sum_{n,k} \frac{1}{2} \text{Trace}G(\mathbf{k} + \mathbf{q}; i \hbar (\omega_n + \nu_m)) \hat{\sigma}^\beta G(\mathbf{k}; i \hbar \omega_m) \hat{\sigma}^\alpha, \]  

where \( \omega_n \) is the nuclear Larmor frequency, and \( A(\mathbf{q}) \) is the averaged strength of the local hyperfine field. The factor \( \text{Im} \chi^{+,-}(\mathbf{q}; \omega) \) represents the density of states for magnetic spin–flip fluctuations. A typical value of the nuclear Larmor frequency is \( \hbar \omega_N \sim 10^{-7} \) meV and so, for all but in systems with exceptionally slow spin–fluctuations, one may approximate \( \omega_N \) by \( \omega_N = 0 \). This approximation could be expected to fail near a quantum critical point.
where \( \omega_n \) are the fermion Matsubara frequencies, \( \hbar \omega_n = \pi k_B T (2n + 1) \) and \( \nu_m \) is a boson Matsubara frequency. For unitary states where \( \tilde{H}_{MF}^2 \) is diagonal, the quasi–particle contribution to the Fourier transformed Green’s function can be written as

\[
G(k; i\hbar\omega_n) = -Z^{-1} \left( \frac{i\hbar \omega_n + \tilde{H}_{MF}}{\hbar^2 \omega_n^2 + E_k^2} \right).
\] (10.255)

Hence, on evaluating Eqn. (10.254) and continuing the imaginary frequency \( i\nu_m \) onto the real \( \omega \) axis, the energy difference components of the imaginary part of the susceptibility tensor are given by the expression,

\[
Im[\chi^{\alpha,\beta}(q; \omega)] = Z^{-2} \pi \left( \frac{g\mu_B}{2} \right)^2 \frac{1}{N} \sum_k \int_{-\infty}^{+\infty} dE \left[ f(E) - f(E + \hbar\omega) \right]
\times \frac{1}{2} \text{Trace} \left( \frac{E + \tilde{H}_{MF}}{4E(E + \hbar\omega)} \right) \tilde{\sigma}^\alpha \left( E + \hbar\omega + \tilde{H}_{MF} \right) \tilde{\sigma}^\beta \left( E + \hbar\omega \right)
\times \left[ \delta(E - E_k) \delta(E + \hbar\omega - E_{k+q}) + \delta(E + E_k) \delta(E + \hbar\omega + E_{k+q}) \right].
\] (10.256)

This represents a quasi–elastic process involving scattering from the thermal population of quasi–particles. The factors in front of the spin operators, as modified by the matrix nature of \( \tilde{\sigma} \), produce the coherence factors. Since the coherence factors differ between the singlet and triplet pairing cases, we shall discuss them separately.

**Singlet Pairing**

In this case, the spin–flip excitation spectrum is obtained as

\[
Im[\chi^{\pm,\mp}(q; \omega)] = \pi Z^{-2} \left( \frac{g\mu_B}{2} \right)^2 \frac{1}{N} \sum_k \int_{-\infty}^{+\infty} dE \left[ f(E) - f(E + \hbar\omega) \right]
\times \left( 1 + \frac{\xi(k)\xi(k + q) + D(k)D(k + q)}{E_k E_{k+q}} \right)
\times \left[ \delta(E - E_k) \delta(E + \hbar\omega - E_{k+q}) + \delta(E + E_k) \delta(E + \hbar\omega + E_{k+q}) \right].
\] (10.257)

The two summations over \( k \) and \( k + q \) in Eqn. (10.250) when combined with Eqn. (10.257) have the effect that the bi–linear term in \( \xi(k) = e(k) - \mu \), which is anti–symmetric about the Fermi energy, vanishes. Also, since for singlet superconductivity, the order parameter is an even function of \( k \) these terms are retained. Then, in the \( s \)–wave phase, the relaxation rate is given
by

$$\frac{h}{T_1} = \pi k_B T Z^{-2} (g \mu_B)^2 A^2 \int_0^\infty dE \left( - \frac{\partial f}{\partial E} \right) \left[ 1 + \left( \frac{\Delta_0}{E} \right)^2 \right] \rho_{BCS}(E)^2,$$

(10.258)

where we have set $\omega_N = 0$, and $A$ is the local hyperfine field. The above expression indicates that a peak in $1/T_1$ should occur just at the superconducting transition. The peak occurs since the BCS density of states diverges at $E = \Delta_0$, which yields a divergence in the integrand in the superconducting state. The logarithmic divergence of $1/T_1$ in the superconducting state is actually suppressed by small residual anisotropy in the gap and also by the quasi–particle lifetimes. As the derivative of the Fermi function

$$\left( - \frac{\partial f}{\partial E} \right) \bigg|_{E=\Delta_0}$$

(10.259)

has its largest value in the superconducting state at $T = T_c$, the above argument indicate that a peak in $1/T_1$ occurs just at $T_c$. The resulting experimentally observed peak is known as the Hebel–Slichter peak [471], and is often seen in weak–coupling $s$–wave superconductors. The peak actually occurs at roughly $0.8 T_c$. This reduced temperature and the suppression of the logarithmic divergence is well described by interactions between thermally excited phonons and the quasi–particles [472]. Fibich found that the temperature dependence of the rate could be expressed as

$$\frac{h}{T_1} \propto 2 k_B T f(\Delta_0) \left[ 1 + \frac{\Delta_0}{k_B T} (1 - f(\Delta_0)) \ln \left( 2 \left( \frac{2\Delta_0}{\Gamma(T)} \right)^{4/3} \right) \right],$$

(10.260)

where $\Gamma(T)$ represents the imaginary part of the gap which is a characteristic energy for quasi–particle scattering from a thermal distribution of phonons, $\Gamma(T) \sim (k_B T)^2 / h \omega_D$. However, in strong–coupling $s$–wave systems, quasi–particle interactions and lifetime effects can substantially suppress the peak. At low temperatures, $T \ll T_c$, the relaxation rate is expected to show a thermally activated temperature variation, $1/T_1 \propto \exp[-\Delta_0 / k_B T]$.

**Triplet Pairing**

The coherence factors in the triplet or $p$–wave pairing phases should be replaced by

$$\left( 1 + \frac{Re[\xi(k)\xi(k+q) - (\hat{z} \cdot \vec{d}(k))(\vec{d}^*(k+q) \cdot \hat{z})]}{E_k E_{k+q}} \right).$$

(10.261)

Since $\xi(k) = e(k) - \mu$ is an odd function about the Fermi energy and $\vec{d}(k)$ is an odd function of $k$, the bi–linear terms vanish, leaving a coherence factor of
unity. Hence, the rate is given in terms of an integration over an appropriate quasi–particle density of states squared for the $p$–wave phase.

$$\frac{\hbar}{T_1} = \pi k_B T Z^{-2} (g \mu_B)^2 A^2 \int_0^\infty dE \left( -\frac{\partial f}{\partial E} \right)^2 \rho_{S=1}(E)^2 . \quad (10.262)$$

We note that the weak logarithmic divergence of the density of states in the ABM phase is integrable, and the Hebel–Slichter peak is also completely absent in the polar phase.

At low temperatures in the BW phase, the same type of exponentially activated behavior is recovered as in the BCS phase. The low temperature form of $1/T_1$ in the ABM phase is given by

$$\frac{\hbar}{T_1} = 4! \pi \frac{(g \mu_B)^2 A^2 Z^{-2} \rho(\mu)^2}{\Delta_0^4} (k_B T)^5 \quad (10.263)$$

and in the polar phase

$$\frac{\hbar}{T_1} = \pi \frac{2^2(g \mu_B)^2 A^2 Z^{-2} \rho(\mu)^2}{2 \Delta_0^4} (k_B T)^3 , \quad (10.264)$$

where the inequality $T \ll T_c$ should hold for both expressions. Thus, the characteristic energy dependence associated with the distribution of nodes could govern the low temperature quasi–particle contribution to the spin–lattice relaxation rate. Also, the quasi–particle contribution to the relaxation rate should remain unrenormalized. However, it should be noted that only the lowest order polarization part of the susceptibility has been considered but the higher order interactions between the quasi–particles and vertex corrections are also important. The vertex corrections may be expected to partially cancel the effect of the self–energy which is responsible for $Z$. The interactions are responsible for adding the low–energy collective spin–fluctuations to the continuum of single quasi–particle Stoner excitations.

The spin–lattice relaxation rates of the heavy–fermion superconductors UBe$_{13}$ [25], UPt$_3$ [473], CeCu$_2$Si$_2$ [475], UPd$_2$Al$_3$ [474] and CeIrIn$_5$ [61, 62] do not show any evidence of a Hebel–Slichter peak at $T_c$, but instead show a cross–over between a linear $T$–like Korringa variation above $T_c$ to an approximate $T^3$ variation in the superconducting state. In UPt$_3$, the $T^3$ law is only followed closely in the restricted temperature range between 0.1 and 0.3 K, which is far below the superconducting transition temperature ($T_c \sim 0.5$ K). However, in UBe$_{13}$, UPd$_2$Al$_3$ and to a lesser extent CeCu$_2$Si$_2$, the $T^3$ dependence holds right up to $T_c$. Since the gap $\Delta_0(T)$ is expected to be rapidly varying with $T$ in this temperature region, the $T^3$ variation should not be interpreted in terms of the power law energy dependence of the quasi–particle density of states. The power law $T$ dependence due to the energy dependence of the quasi–particle density of states is expected to be restricted to occur in a temperature regime far below $T_c$. In UBe$_{13}$, the approximate $T^3$
variation crosses over to a linear $T$ variation at the lowest measured temperatures [476]. The coefficient of the linear $T$ term is observed to increase with doping [464], which is consistent with the picture of a gapless superconducting phase caused by resonant impurity scattering of Cooper pairs with non–zero angular momentum, $l \neq 0$. Although no low temperature linear $T$ regimes were identified in the relaxation rates of UPd$_2$Al$_3$ [474], CeCu$_2$Si$_2$ [475] and CeCoIn$_5$ [61], at the lowest measured temperatures, the data do show indications of departures from the $T^3$ power law variation which are consistent with linear $T$ variations.

**Neutron Scattering Cross–section**

Perhaps one of the potentially most powerful probes of the nature of the order parameter would be inelastic neutron scattering measurements. The scattering cross–section not only provides a measure of the spectrum of the magnetic fluctuations of the quasi–particles but also, via the dependence on polarization and the direction of the momentum transfer $\hbar \mathbf{q}$, the anisotropy in the coherence factors. The main limitations of this method are due to the strong residual interactions between the quasi–particles that result in the large amplitude spin–fluctuations, and the loss of intensity needed for polarized scattering. The gaps that could be observed in the inelastic neutron scattering cross–section may be expected to be of the order of $2\Delta_0$ which, for the heavy–fermion superconductors, could be expected to range between 0.3 meV and 1 meV.

The magnetic scattering cross–section of an incident beam of unpolarized neutrons is related the imaginary part of the dynamic susceptibility via,

$$\frac{d^2\sigma}{d\omega d\Omega}(\mathbf{q}; \omega) = \gamma_0^2 \frac{k_f}{k_i} \frac{|F(q)|^2}{g^2 \mu_B} [1 + N(\omega)] \sum_{\alpha,\beta} \text{Im} \left[ \chi^{\alpha,\beta}(q; \omega) \right] (\delta_{\alpha,\beta} - \hat{q}_\alpha \hat{q}_\beta) ,$$

(10.265)

where $\hbar \mathbf{q}$ and $\hbar \omega$ refer to the momentum and energy transfer of the neutron, and $F(q)$ is the atomic form factor. The summation over $\beta$ corresponds to experiments in which the polarization of the scattered beam is not observed. It should be noted that the dipole nature of the interaction between the neutron and the electron spins results in the neutron only interacting with the spin components transverse to the momentum transfer $\mathbf{q}$. The imaginary part of the dynamic susceptibility contains the Raman scattering type of process expressed in Eqn. (10.256), and a pair–breaking scattering process. The quasi–elastic or Raman scattering process involves the scattering of the neutrons from thermally excited quasi–particles. These low–energy fluctuations formed the basis for the discussion of NMR experiments, and are expected to vanish in the limit of zero temperature. The spectrum originating from processes in which pairs in the condensate are broken and where the resulting quasi–particles are then scattered across the gap is given by the energy sum terms in Eqn. (10.254). These terms remain finite at zero temperature. The
energy loss contribution to the pair–breaking process is evaluated as

\[ \text{Im} \left[ \chi^{\alpha,\beta}(q, \omega) \right] = Z^{-2} \pi \left( \frac{g \mu_B}{2} \right)^2 \frac{1}{N} \sum_k \left[ 1 - f(E_k) - f(E_{k+q}) \right] \]

\[ \times \frac{1}{2} \text{Trace} \left( \frac{(E_k - \tilde{H}_{MF})\tilde{\sigma}^{\beta}(E_{k+q} + \tilde{H}_{MF})\tilde{\sigma}^{\alpha}}{4E_k E_{k+q}} \right) \delta(h\omega - E_k - E_{k+q}). \]

Here, we have only considered the quasi–particle contribution. The value of the trace depends upon the character of the superconductivity. Again, we consider the singlet pairing case separately from triplet pairing.

**Singlet Pairing**

Conventional singlet pairing superconductors are paramagnetic, so one retains spin rotational invariance

\[ \frac{1}{2} \text{Im} \left[ \chi^{+,+}(q, \omega) \right] = \text{Im} \left[ \chi^{-,+}(q, \omega) \right] = \text{Im} \left[ \chi^{-,x}(q, \omega) \right] = \text{Im} \left[ \chi^{y,y}(q, \omega) \right]. \]

The imaginary part of the quasi–particle susceptibility is found as

\[ \text{Im} \left[ \chi^{+,+}(q, \omega) \right] = \pi (g \mu_B)^2 Z^{-2} \frac{1}{N} \sum_k \left[ 1 - f(E_k) - f(E_{k+q}) \right] \]

\[ \times \left( \frac{(E_k - \xi(k))(E_{k+q} + \xi(k + q)) - D(k)D(k + q)}{4E_k E_{k+q}} \right) \delta(h\omega - E_k - E_{k+q}). \]

The scattering cross–section for pair–breaking scattering processes vanishes identically in the limit \( q \to 0 \) so, for this \( q \) value, neutron scattering only occurs through processes involving the Raman scattering from thermally activated quasi–particles. In this limit, the non–zero part of the quasi–particle contribution involves coherence factors of unity and would manifest itself by a narrow zero energy delta function like peak with strength proportional to \( Z^{-1} \), in the absence of spin–orbit scattering.

For finite \( q \), the cancellation in the coherence factors for the pair breaking processes is incomplete. For \( s \)–wave pairing, the pair breaking process has a threshold at the maximum value of the superconducting gap \( \hbar \omega = 2 \Delta_0 \), for \( 0 < q < 2 k_F \). For non \( s \)–wave pairing phases where there are nodes in the order parameter, interesting possibilities occur when the system is close to an antiferromagnetic instability. In this case, one expects that in the normal state, there should be a quasi–elastic peak from magnetic fluctuations that should show softening at the \( q \) value \( Q_c \) which corresponds to the magnetic Bragg peak of the (hypothetical) ordered state [477]. The magnetic fluctuations are expected to decay into quasi–particle excitations. Therefore, the
height and width of the quasi–elastic peak is governed by the quasi–particle density of states. As the temperature is lowered and the normal state becomes unstable to a superconducting state, the low–energy quasi–particle density of state is suppressed since the superconducting gap opens up on portions of the Fermi surface. This may result in the quasi–elastic neutron scattering peak at \( Q_c \), transforming into a narrow low–energy resonance for \( \hbar \omega < 2 \Delta_0 \). The height of the peak is expected to have an inverse correlation with the maximum value of the superconducting gap. Furthermore, the \( \omega \) dependence of the low–energy edge of the resonance should either show a \( \omega \) or \( \omega^2 \) variation depending upon the existence of either line nodes or point nodes in the gap. The sharp peak is expected to rapid broaden and disperse to higher energies as \( q \) is varied away from \( Q_c \). Excitations of a similar type have been observed in the superconducting state of magnetically ordered UPd\(_2\)Al\(_3\) [347,349,436,478]. The spectra of the transverse excitations found in the polarized inelastic neutron scattering spectra, at \( q = Q_c \), are shown in Fig. 10.74.

**Triplet Pairing**

The pair breaking scattering cross–section for triplet superconductors is governed by

\[
\text{Im} \chi_{ij}^i(q;\omega) = \pi (g \mu_B)^2 Z^{-2} \frac{1}{N} \sum_k \left[ 1 - f(E_k) - f(E_{k+q}) \right] \delta(\hbar \omega - E_k - E_{k+q})
\times \text{Re} \left( \frac{(E_k - \xi(k))(E_{k+q} + \xi(k+q)) + \bar{d}(k)d^*(k+q)}{4E_k E_{k+q}} - 2d_i(k)d^*_i(k+q) \right).
\]

(10.269)

In the limit \( q \to 0 \), the coherence factors relevant to unpolarized experiments remain finite, in contrast with the singlet phase. This is because the vector \( \bar{d} \) takes over the role of the momentum transfer \( q \), in defining the coupling of the neutron’s spin to the electronic magnetic moments. The energy dependence of the various limiting forms of the unpolarized neutron cross–section are given by

\[
\propto \pi \rho(\mu) \frac{\Delta_0^2}{\hbar \omega} \frac{2}{\sqrt{\hbar^2 \omega^2 - 4 \Delta_0^2}} , \quad \hbar \omega \geq 2 \Delta_0 ,
\]

(10.270)

for the BW phase,

\[
\propto \frac{\pi \rho(\mu)}{4 \hbar \omega \Delta_0} \left[ \hbar^2 \omega^2 + 4 \Delta_0^2 \right] \ln \left[ \frac{\sqrt{\hbar \omega + 2 \Delta_0}}{\sqrt{\hbar \omega - 2 \Delta_0}} - \frac{\Delta_0 \hbar \omega}{2} \right]
\]

(10.271)
In the ABM phase, while the polar phase cross-section is proportional to

\[ \propto \frac{\pi^2 \rho(\mu) \hbar \omega}{8 \Delta_0}, \quad 2\Delta_0 \geq \hbar \omega \]

\[ \propto \pi \rho(\mu) \left( \sin^{-1} \frac{2\Delta_0}{\hbar \omega} - \frac{2\Delta_0}{\hbar^2 \omega^2} \sqrt{\hbar^2 \omega^2 - 4\Delta_0^2} \right), \quad 2\Delta_0 \leq \hbar \omega. \]  

These are shown in Fig. 10.75. The non-analyticities stem from the characteristic energy dependences of the quasi-particle density of states. The \( q = 0 \) spectra could lead to a unique identification of triplet superconducting phases, however, neutron scattering experiments at low momentum transfers are difficult to perform. Therefore, the observation of the energy and momentum dependences of low-energy resonances corresponding to the quasi-elastic paramagnon or anti-paramagnon excitations of the normal state.
Fig. 10.75. The calculated $T \to 0$ limit of the imaginary part of the uniform ($q = 0$) frequency dependent susceptibility of $p$-wave superconducting phases, normalized to the density of states at the Fermi energy. The BW phase exhibits a square root singularity at $\hbar \omega = 2\Delta_0$. The imaginary part of the $q = 0$ dynamic susceptibility for the ABM phase exhibits a square root singularity at the maximum gap and a $\omega^2$ variation at low frequencies. The polar phase shows a linear $\omega$ variation at low frequencies.

could be used to determine the nature of superconducting states. In particular, in triplet superconductors, there exists a possibility for observing a double–peaked structure in the low–energy magnetic response, corresponding to the different behavior of magnetic fluctuations perpendicular and parallel to the vector superconducting order parameter.

10.5 Heavy Fermion Superconducting Compounds

Elsewhere in this chapter, the underlying theoretical and experimental approaches to the problem of heavy fermion superconductivity are discussed in detail. In this section we consider the heavy fermion superconductors on a compound–by–compound basis. For each compound we provide a brief introduction and an overall “snapshot” of the physical picture that is developing for each compound at the time this review was written (mid 2003). Our focus is on the nature and origin of the superconducting states themselves. One cannot, of course, completely understand the superconducting states without a clear understanding of the normal state that they arise from, so the fact that the heavy fermion problem has not yet been solved represents an intrinsic limitation in our endeavor. We assume that the reader is familiar with the
general characteristics of the heavy fermion state either from reading other sections in this chapter or from any of the excellent review articles that exist such as those by Stewart [480], Hess, Riseborough, and Smith [481], or Grewe and Steglich [302] for example.

In a recent review article focused on the heavy fermion superconductors, Brison et al. [482] (citing an earlier review by Ott [483]) identify the central questions in the field, questions that date from the earliest heavy fermion superconductors studied:

- Does the pairing mechanism involve magnetic interactions?
- What is the symmetry of the superconducting order parameter and the topology of the gap function?
- What is the nature of the interplay between magnetic order (when it exists) and superconductivity?

In another recent review of unconventional pairing in superconductors Annett [484] identifies five “classes” of experimental evidence for unconventional superconductivity:

- Class 1: Experiments consistent with a multi–component order parameter, such as those experiments showing multiple superconducting phases in UPt$_3$ (Ref’s [14] and [44] for example). These experiments constitute “definitive proof” of an unconventional superconducting state.
- Class 2: Experiments that measure the macroscopic order parameter symmetry, such as Josephson interference effects. Such experiments have been very useful in studies of the cuprates. Several heavy fermion compounds show Josephson critical currents. Measurements consistent with anisotropic order parameters exist but overall these difficult experiments have not yet been accomplished in the heavy fermion compounds as successfully as in the cuprates.
- Class 3: Measurements of the electronic spin susceptibility in the superconducting state which tends to zero as $T \rightarrow 0$ for singlet pairing and remains finite for triplet or higher order pairing, measurements such as the Knight shift of thoriated UBe$_{13}$ [485, 486] for example.
- Class 4: Experiments demonstrating that the Fermi surface average of the gap function is zero (usually through the failure of Anderson’s theorem), experiments such as resistivity measurements probing the sensitivity of $T_c$ to non–magnetic impurities. If the average is non–zero, Anderson’s theorem can be applied and the superconducting state is not easily destroyed by non–magnetic impurities. Results consistent with this effect have been reported for UPt$_3$ [487, 488].
- Class 5: Experiments consistent with the gap function vanishing at line and/or point nodes on the Fermi surface. Such a structure results in power–law temperature dependences for a host of measurable quantities such as the specific heat, ultrasonic attenuation, or thermal conductivity [489]. Such power–law dependences (as opposed to the exponential
temperature dependence associated with a uniform $s$–wave gap) are ubiquitous in the heavy–fermion superconductors.

### 10.5.1 Uranium Compounds

**UPt$_3$**

Since the discovery of superconductivity by Stewart *et al.* [6], UPt$_3$ has arguably become the most extensively studied of all the heavy fermion superconductors. It now seems safe to assert that unconventional superconductivity in UPt$_3$ has been unambiguously established. A comprehensive review on UPt$_3$ by Joynt and Taillefer [378] has recently appeared, it contains an extensive survey of the literature and an in–depth analysis of the state of contemporary research.

Superconductivity in hexagonal UPt$_3$ ($T_c^+ = 0.53$ K) condenses out of a “heavy” normal state characterized by a resistivity that decreases monotonically with falling temperature and a spin fluctuation–like term in the specific heat, both of which are unusual in heavy fermion superconductors. Experiments show that UPt$_3$ is an extreme Type II superconductor (with a Ginzburg–Landau parameter of about 44 in the A–phase) in the clean limit [378].

A tendency toward magnetism manifests as a peak in the magnetic susceptibility near 18 K which evolves into a metamagnetic transition near 20 T at low temperatures. A subtle, small–moment ($\sim 0.02 \mu_B/U$–atom oriented along a$^*$ in the basal plane with domain sizes of about 150 Å), antiferromagnetic order appears at $T_N \sim 5$ K which seems to be intimately related to the superconducting phase diagram as discussed below. The inability to detect a feature associated with $T_N$ using techniques other than neutron scattering (such as $\mu$SR, NMR, or virtually any thermodynamic measurement) suggests that the moments are not static, but fluctuate at a very high rate [491].

UPt$_3$ exhibits three distinct superconducting phases: the A phase occurs at the onset of superconductivity in ambient fields, the B phase appears at $T_c^- = T_c^+ - 50$ mK, below the onset of the A phase and extends to $T = 0$ (the B–phase is the ground state). The proximity of $T_c^+$ and $T_c^-$ suggests that they may arise from degenerate states split by some perturbation, the most likely candidate being the antiferromagnetic order. The C phase exists in magnetic fields above about 0.4 T. (One could argue that there are, in fact, five phases since the A and B phases each have a Meissner state below $H_{c1}$ and a vortex state above $H_{c1}$.) A schematic of the high field superconducting phase diagram is shown in Fig. 10.76, the four phase boundaries shown meet at a true tetracritical point near (0.38 K, 0.8 T) with $H \parallel c$ and (0.43 K, 0.8 T) with $H \perp c$. Also shown in Fig. 10.76 are figures characterizing the gap structures of the $E_{2u}$ model [492], a solid candidate for the multi–component order parameter characterizing the superconducting states of UPt$_3$ in terms of spin–triplet, $f$–wave pairing. This approach describes the unusual shape...
and anisotropy of the upper critical field very well with paramagnetic limiting for fields along the c-axis [493].

The interplay between superconductivity and magnetism is demonstrated most clearly by neutron-scattering and specific heat experiments under pressure: the antiferromagnetism is suppressed while the two superconducting transitions at $T_c^+$ and $T_c^-$ appear to merge into one. Within experimental resolution, the superconducting transitions merge at the same pressure (about 3 kbar) that destroys antiferromagnetism [46], a most compelling result.

Candidate theories for the order parameter of UPt$_3$ include two-dimensional representations where a small coupling to the antiferromagnetism splits the energies of two degenerate states, mixed representations where the two zero field superconducting transitions involve gap functions that are not related by symmetry (so the splitting of $T_c^+$ and $T_c^-$ is “accidental”, unrelated to the antiferromagnetism), and others. Virtually all of the candidate theories result in an odd-parity order parameter; the reader is referred to Joynt and Taillefer [378] for an in-depth discussion.

The identification of the pairing mechanism remains one of the most important and least understood aspects of the work on the heavy fermion superconductors in general and the situation for UPt$_3$ is no exception. It is generally assumed that mechanism involving the exchange of spin fluctua-
tions, similar to that of superfluid $^3$He [137], and that the Cooper pairs are in a triplet state.

**UBe$_{13}$**

UBe$_{13}$ (along with CeCu$_2$Si$_2$ and other heavy fermion superconductors that also show a magnetic phase transition) is frequently characterized as a non–Fermi Liquid superconductor [497] because the superconducting state appears (near $T_c = 0.9$ K) before Fermi liquid behavior has a chance to set in (though the application of modest pressures and/or magnetic fields causes the Fermi liquid state to emerge above $T_c$ [499]). Of all the known heavy fermion superconductors UBe$_{13}$ has the largest effective mass and one of the few compounds with cubic symmetry. UBe$_{13}$ does not appear to order magnetically, though there is some evidence for field–induced small–moment magnetism coexisting with the superconducting state above about 5 T it has not been confirmed [500]. The resistivity of UBe$_{13}$ is enormous, near 100 $\mu \Omega$–cm just above $T_c$, leading to an electronic mean–free–path of only a few lattice spacings in length and (not surprisingly) dirty–limit superconductivity.

Many of the initial measurements on UBe$_{13}$, such as the specific heat, NMR spin–lattice relaxation rate, and London penetration depth exhibit power–law temperature dependences suggesting the presence of line–nodes in the gap function. Tunneling measurements have also resulted in evidence for Andreev surface bound–states [447]. More recent measurements of the specific heat and thermal expansion on higher quality single crystals show an unusual temperature dependence suggestive of a line of “anomalies” in the H–T plane that has been interpreted in terms of antiferromagnetic fluctuations associated with a quantum critical point [497]. This behavior is especially intriguing in samples doped with thorium, a subject we will return to in another section.

Measurements of the lower critical field show the quadratic temperature dependence characteristic of a conventional superconducting state, but the shape of the upper critical field is quite unusual, exhibiting significant positive curvature in the best samples. Recent measurements of the upper critical field under pressure yield a series of $H_{c2}(T,P)$ curves that are well fit by a strong coupling theory incorporating an FFLO state in high magnetic fields. These results are also consistent with a non–phonon–mediated coupling mechanism [380].

Evidence for unconventional superconductivity in UBe$_{13}$ is mounting but the nature of the anomalies described above have yet to be incorporated into a coherent picture of the superconducting state.

**Thoriated UBe$_{13}$**

The phase diagram of U$_{1-x}$Th$_x$Be$_{13}$ is shown in Fig. 10.3. Doping non–magnetic thorium onto the uranium sites depresses $T_c$ non–monotonically and a second phase transition appears at a lower temperature ($T_{c2}$) in the thorium concentration range of about 2% to 4%. Though not as well established experimentally as the multiple superconducting phase diagram of UPt$_3$, pres-
sure studies, lower critical field measurements (showing a sharp upward kink at $T_{c2}$ [36]) and the size of the specific heat jumps suggest that the colder phase transition separates one kind of superconducting state from another. On the other hand, the observation of small moment magnetism below $T_{c2}$ ($\mu \sim 10^{-3} \mu_B/\text{U-atom}$ [33]) suggests that this lower state may be magnetic, perhaps a spin–density–wave state coexisting with the superconductivity.

Recent studies of the phase diagram utilizing both specific heat and thermal expansion measurements are shown in Fig. B where the open symbols denote the “anomalies” discussed in the section on pure UBe$_{13}$ and the solid symbols represent phase transitions [497]. There is an intriguing correlation suggesting that the anomalies in the pure compound evolve into the colder phase of the thoriated compounds. Also shown in Fig. B is a vertical solid line near a thorium concentration $x_{c1} \approx 0.02$ representing the pressure studies of Zieve et al. [501] who find clear evidence for a vertical phase boundary separating the two regions.

Theoretical efforts to understand this unusual phase diagram include multiple superconducting states and the onset of antiferromagnetism [502], broken time–reversal symmetry at $T_{c2}$ [503], a “freezing” of the antiferromagnetic fluctuations associated with proximity to a quantum critical point [497], and a “ferrisuperconductivity” theory involving a multi–component order parameter and the appearance of a charge density wave state at $T_{c2}$ [504].

**URu$_2$Si$_2**

Tetragonal URu$_2$Si$_2$ enters the superconducting state near 1.5 K, a temperature about ten times colder than the temperature where it enters into a state of “hidden order”. The term “hidden order” denotes an unknown phase with which the superconductivity coexists and which is presently the subject of much current study and debate. Long thought to be a transition to a small–moment ($\mu = 0.03 \mu_B/\text{U-atom}$) antiferromagnetic state, it has also been recognized for a long time that the size of the specific heat jump is much larger than one would expect for such a transition. Recent neutron diffraction [226] and NMR measurements under pressure [225] have led to the suggestion that the magnetism is from a minority phase, though this matter is still under active discussion [505]. A resolution of this issue will impact our understanding of the superconducting state which, according to recent neutron scattering measurements, is coupled to the magnetic order [506].

Evidence for unconventional superconductivity manifests in specific heat measurements consistent with a line of nodes in the gap function [507] and by anisotropic point contact measurements of the Josephson current between URu$_2$Si$_2$ and Nb, a result which suggests that the order parameter must have even parity [455] (*e.g.* $d$–wave). The upper critical field is strongly anisotropic, strongly Pauli limited along the $c$–axis, and exhibits a positive curvature consistent with $d$–wave symmetry [508]. It has been pointed out that this interpretation violates the symmetry required of a simple antiferromagnet [509], but with recent measurements suggesting that the magnetism may not
be intrinsic the original argument remains an important part of the picture of unconventional superconductivity developing for this compound [510].

**UPd$_2$Al$_3**

The superconducting state of UPd$_2$Al$_3$ condenses near $T_c = 2.0$ K out of a coexisting antiferromagnetic state ($T_N = 14.5$ K) with atomic–like moments ($\mu = 0.85 \mu_B$/U–atom) aligned in the hexagonal basal plane [51, 344, 511]. NMR measurements of the nuclear relaxation time [512] and the thermal conductivity [513] are consistent with a line of nodes in the gap function, while Knight shift measurements and a Pauli limited upper critical field indicate even parity pairing [514]. But the most important development in UPd$_2$Al$_3$ derives from the fact that relatively high quality thin films, with a $T_c$ near 1.6 K only slightly reduced from the bulk $T_c$, have been fabricated for tunnelling experiments. These experiments reveal a strong coupling to an excitation whose energy nearly matches a magnetic excitation clearly visible in neutron scattering measurements [434, 478]. Taken together, these exciting experimental results constitute the strongest evidence for a magnetic mechanism (in this case magnetic excitons) for superconductivity yet discovered.

**UNi$_2$Al$_3**

Though similar in many respects to isostructural UPd$_2$Al$_3$, there are clear differences in the unconventional superconducting state of UNi$_2$Al$_3$. Superconductivity appears near 1 K and coexists with an incommensurate spin density wave state with a (relatively) small magnetic moment (about $0.2 \mu_B$/U–atom) that appears near 4.5 K [515, 516]. As with the Pd compound, NMR measurements of the temperature dependence of $T_1$ suggest the presence of line nodes in the gap [517]. The upper critical field of UNi$_2$Al$_3$ is well fit by the conventional WHHM theory without paramagnetic limiting [518, 519] while measurements of the Knight shift show that the spin susceptibility does not change on crossing $T_c$ and down to 50 mK [470], both of these results are consistent with a spin–triplet superconducting state.

**U$_2$PtC$_2**

The lowest effective mass of all the heavy fermion compounds we discuss belongs to U$_2$PtC$_2$ which may be considered as intermediate between the heavy fermion superconductors and less–anomalous uranium based superconductors such as U$_6$Fe. Though the critical temperature is appreciable ($T_c = 1.47$ K) we are unaware of any clear evidence for unconventional superconductivity in this compound owing to a lack of experimental studies.

### 10.5.2 Cerium Compounds

**CeCu$_2$Si$_2**

Tetragonal CeCu$_2$Si$_2$ was the first heavy fermion superconductor discovered [3]. The close proximity of superconductivity and magnetism in CeCu$_2$Si$_2$ is highlighted by the sensitivity of the ground state to the details of sample preparation and stoichiometry. Quite a bit of work was required to sort out
the ground state which can be either bulk superconducting (S-type), magnetic (A-type), both (A/S-type), or “a related phase” (X-type) which is probably magnetic; there is also a high field magnetic phase (the B-phase) and recent high field magnetization studies are consistent with the A and B phases being spin density wave phases [494]. The best single crystals are of the A/S type [495] which becomes superconducting at 0.68 K just below the onset of the magnetic A-phase at 0.70 K. $\mu$SR measurements show that the superconducting state competes with the magnetic state (consistent with an SDW state which will compete with superconductivity for the Fermi surface) and that the two states do not coexist microscopically [309]. Given this proximity of low temperature states it is not surprising that CeCu$_2$Si$_2$ exhibits non-Fermi Liquid behavior in its specific heat and electrical resistivity [192]. It is also not surprising that the superconducting properties of CeCu$_2$Si$_2$ show significant sample dependences.

In studies of several off-stoichiometry single crystal samples of CeCu$_2$Si$_2$, the anisotropic upper critical fields can sometimes be fit by a standard $s$-wave model with significant Pauli limiting and sometimes not [388] though the overall shape is qualitatively consistent with conventional superconductivity. The superconductivity of CeCu$_2$Si$_2$ is in the clean limit and exhibits a strong Type II character with a typical Ginzburg–Landau parameter in the 50–56 range.

Early studies of the superconducting states of a wide range of samples do not show significant evidence for unconventional superconductivity [388]. A more recent study, however, shows evidence for two different kinds of superconducting states from samples with only slightly different stoichiometry. The two sample groups show a $T^2$ dependence for the superconducting specific heat but opposite pressure dependences for $T_c$. $d$-wave superconductivity has been proposed [496].

CeRhIn$_5$

The tetragonal crystal structure of CeRhIn$_5$ (and that of CeIrIn$_5$ and CeCoIn$_5$ discussed below) can be thought of as layers of CeIn$_3$ separated by layers of RhIn$_2$ leading to a quasi–two–dimensional electronic structure. Some features of this sub–family of heavy fermion superconductors, such as a proximity to antiferromagnetism, may therefore be similar to the cuprate superconductors [57]. However, unlike the isostructural compounds CeIrIn$_5$ and CeCoIn$_5$ (both of which are heavy fermion superconductors at ambient pressure), CeRhIn$_5$ is a heavy fermion antiferromagnet at ambient pressure with a Néel temperature $T_N = 3.8$ K. In the antiferromagnetic state the Ce spins (0.8 $\mu_B$/Ce–atom [58]) form a helical structure along the $c$–axis, a structure characterized by an incommensurate wave vector [520]. The magnitude of the internal field created by the Ce spins decreases linearly with applied pressure while $T_N$ remains nearly constant [521]. At a critical pressure near $P_c \sim 15$ kbar specific heat measurements suggest that the antiferromagnetic state is abruptly replaced by a superconducting state whose critical temper-
ature (about 2.1 K) is surprisingly pressure independent [522]. More recent NQR measurements show that the two states coexist homogeneously at a pressure of 17.5 kbar. At 21 kbar the spin–lattice relaxation rate exhibits a $T^3$ temperature dependence and no coherence peak, suggesting a line node in the gap function. A $T^2$ term in the superconducting specific heat is also consistent with line nodes [522].

**CeIrIn$_5$**

Nearly antiferromagnetic CeIrIn$_5$ shows quadratic and linear temperature dependences of the superconducting specific heat and thermal conductivity (in the “universal limit”) respectively [59] along with a $T^3$ temperature dependence of the spin–lattice relaxation rate with no Hebel–Slichter coherence peak [61, 62]. All of these experimental results are consistent with line nodes in the gap function. The upper critical field is anisotropic but of a conventional shape that does not yield strong experimental evidence either for or against Pauli limiting [523].

**CeCoIn$_5$**

Just at the edge of an antiferromagnetic quantum critical point, tetragonal CeCoIn$_5$ exhibits the highest critical temperature ($T_c = 2.3$ K) of the heavy fermion superconductors and an enormous specific heat jump at $T_c$. Several experimental results are consistent with line nodes in the energy gap: $T^2$ and $T^3$ temperature dependences of the superconducting specific heat and thermal conductivity respectively [59] and a $T^3$ temperature dependence of the spin–lattice relaxation rate with no Hebel–Slichter coherence peak [61]. The Knight shift decreases for both parallel and perpendicular directions to the tetragonal $c$ axis in the superconducting state, which shows that the spin susceptibility decreases with decreasing temperature consistent with spin singlet pairing [61]. A $d_{x^2-y^2}$ state has been proposed for CeCoIn$_5$ based on thermal conductivity measurements which reveal a fourfold symmetry in the a–b plane, characteristic of a superconducting gap with nodes along the ($\pm \pi, \pm \pi$) directions [60]. Also consistent with such a state, several groups report that the phase transition at $H_c2$ is first–order in high fields [60, 525].

The lower critical field shows a linear temperature dependence [526], while the upper critical field exhibits an unusual low temperature shape and hysteresis [527]. Both critical fields are anisotropic. Strong indications of an FFLO state in CeCoIn$_5$ [525] have been confirmed with the observation of a second–order phase boundary just below $H_c2$ at low temperature [528].

**CeIn$_3$**

It is not unreasonable to think of cubic CeIn$_3$ as the parent compound of the previous three heavy fermion superconductors. Under ambient pressure CeIn$_3$ is a heavy fermion antiferromagnet with an ordering temperature $T_N = 10.2$ K, an ordered moment of 0.65 $\mu_B$/Ce–atom, and a wave vector in the [111] direction [529]. As pressure is applied $T_N$ is depressed and eventually vanishes near a temperature of about 0.18 K at a critical pressure of about 26 kbar, below this temperature antiferromagnetism is replaced by a super-
conducted state [530]. This P–T phase diagram, similar to that observed in several high–$T_c$ compounds, has been shown to be characteristic of magnetically mediated superconductivity [530]. Measurements of the spin–lattice relaxation time at a pressure of 26.5 kbar do not show a coherence peak [531] though the upper critical field (at the same pressure) can be described by a conventional strong coupling model in the clean limit [64]. Existing experimental results are not inconsistent with unconventional superconductivity in this important compound, especially given its P–T phase diagram, but, as with most of the heavy fermion superconductors (especially those below), more work is required to identify the symmetry of the order parameter.

**CePd$_2$Si$_2$**

Evolving from a heavy fermion antiferromagnet to a heavy fermion superconductor under applied pressure, the P–T phase diagram of CePd$_2$Si$_2$ is similar to that of CeIn$_3$ and suggests that the superconductivity of CePd$_2$Si$_2$ is also magnetically mediated [530]. The disappearance of antiferromagnetism does not quite coincide with the maximum superconducting critical temperature (as it does in CeIn$_3$) of about 0.52 K which occurs near an applied pressure of 5 GPa. The shape of the upper critical field at this pressure is not inconsistent with conventional superconductivity though there appear to be some deviations at the lowest temperatures [532]. Another study shows that the upper critical field is well described by a weak–coupling, clean–limit model with a slightly anisotropic orbital limit and a strongly anisotropic paramagnetic one [533].

**CeRh$_2$Si$_2$**

The P–T phase diagram of CeRh$_2$Si$_2$ is qualitatively similar to that of CePd$_2$Si$_2$ and CeIn$_3$ (discussed above) where antiferromagnetism (ambient pressure $T_N = 36$ K) is replaced by superconductivity near a critical pressure of 9 kbar and a critical temperature of 0.35 K [68]. The upper critical field is not inconsistent with that of a conventional Type II superconductor though the transition widths are wide and the data are sparse.

**CeCu$_2$Ge$_2$**

Superconductivity at very high pressures has been reported for CeCu$_2$Ge$_2$. Similar to other Ce compounds discussed above, the antiferromagnetic order ($T_N = 4.7$ K at ambient pressure) is suppressed between 7 and 10 GPa and is replaced by a superconducting state which appears below a temperature of about 0.6 K. The critical temperature is nearly pressure independent up to about 13 GPa after which it increases rapidly to a maximum value of almost 2 K near 16 GPa before vanishing near 20 GPa [534]. The upper critical field shows significant Pauli limiting consistent with singlet pairing [535].

### 10.5.3 Praseodymium Compounds

**PrOs$_4$Sb$_{12}$**

Discovered just last year, cubic PrOs$_4$Sb$_{12}$ is the only known Pr based heavy fermion superconductor so far. Thermal conductivity [536] and specific
heat [537] measurements suggest the presence of two distinct superconducting states featuring point–nodes in the gap function (an unusual feature in heavy fermion superconductors). No Hebel–Slichter peak is observed in the temperature dependence of the spin–lattice relaxation time, although an exponential temperature dependence at low temperatures suggests that the gap function is isotropic [538]. An exponential temperature dependence is also found for the magnetic penetration depth as deduced from μSR measurements [539]. A small internal magnetic field, appearing just below $T_c$ is clearly visible in the μSR measurements of Aoki et al. [540], consistent with a multi–component order parameter which, in turn, is consistent with multiple superconducting states. The upper critical field is of a conventional shape and does not show evidence of Pauli limiting [541]. The lower critical field, on the other hand, exhibits a pronounced positive curvature even at the lowest temperatures [542]. Lastly, we note that the presence of a field–induced antiferro–quadrupolar ordered phase just above the upper critical field suggests that quantum quadrupole fluctuations of the Pr ions may play a role in the superconducting mechanism.

10.5.4 Related Materials

Lastly, we discuss several superconductors that are not usually considered to be heavy fermion superconductors but which show a “family resemblance” in the sense that all are examples of superconductivity in strongly correlated electron systems.

**UGe$_2$, URhGe, and ZrZn$_2$**

The topic of ferromagnetic superconductivity might be said to date from 1957 and the seminal work of Ginzburg [544]; a number of excellent reviews covering the work of the intervening decades exist [545] most recently by Flouquet et al. [546]. A most intriguing possibility for the following compounds is that superconductivity and ferromagnetism involve the same electrons.

Superconductivity in orthorhombic UGe$_2$ appears near a pressure of 12 kbar just below the pressure at which ferromagnetism is suppressed [65]. The maximum critical temperature $T_c = 0.7$ K occurs at 12 kbar where the Curie temperature is still about 30 K and the size of the ordered moment is about 1 μB/U–atom. Estimates of the internal field created by the ferromagnetic order are of order 100 T so triplet pairing seems likely. The shape of the upper critical field is anisotropic and strongly pressure dependent, exhibiting reentrant behavior near a pressure of 13.2 kbar [547]. A $p$–wave superconducting state has been proposed that coexists with the itinerant ferromagnetism [548].

At ambient pressure, ferromagnetism appears at 9.5 K in orthorhombic URhGe followed by superconductivity near 0.3 K [67]. The upper critical field of a polycrystal exhibits a conventional shape. Triplet superconductivity is expected given the large internal fields associated with the 0.5 μB/U–atom moments.
Cubic ZrZn$_2$ has been reported to be an ambient pressure superconductor ($T_c = 0.3$ K) where the superconductivity appears out of an itinerant ferromagnetic state ($T_C = 28.5$ K with an ordered moment of 0.17 $\mu_B$/f.u.) [549]. The upper critical field shows a qualitatively conventional shape. Recent theoretical work suggests a multi–component order parameter with nodes in the gap function [551], but the reader is cautioned that very recent work suggests that the superconductivity may be due to surface effects and is not a property of bulk ZrZn$_2$ [550]. Clearly a great deal of work remains to be done to characterize the superconducting states of these intriguing compounds.

PuCoGa$_5$

The final compound we discuss in this section is the tetragonal plutonium–based compound PuCoGa$_5$ which exhibits the highest critical temperature ($T_c = 18.5$ K) ever observed for an f–electron compound [76]. PuCoGa$_5$ (and PuRhGa$_5$ which is reported to superconduct at 8.7 K [552]) exhibits the same crystal structure as the Ce 1–1–5 compounds discussed above, aspects of the Fermi surface structure are also quite similar [553]. Recent electronic structure calculations suggest that the superconductivity is caused by the pairing of plutonium 5f electrons [554]. Measurements of the upper critical field near $T_c$, fit to a conventional WHHM form, suggest that the critical field reaches 74 T at $T = 0$ which would exceed the Pauli limit. The lower critical field at 5 K is estimated to be about 350 Oe which, in turn, permits an estimate of 32 for the Ginzburg–Landau parameter.

We close this section by referring to Table(10.11) containing various superconducting parameters of the heavy fermion superconductors we have discussed above. The significant number of empty spaces is just one piece of evidence suggesting the opportunities still awaiting experimentalists in this mature yet steadily growing field of research.

10.6 The Conclusion

Superconductivity is one of nature’s most ubiquitous collective phenomena in many-particle systems. Superconductivity in metals was explained by the theory of Bardeen, Cooper, & Schrieffer (BCS) in 1957. The basic picture was the notion of Cooper pairing where two fermions (electrons in metals) can form a bound pair in a relative s-wave state (conventional superconductivity) in the neighborhood of the Fermi surface. The interaction that causes the binding is the exchange of a boson (a phonon in a metal) between the fermions, which is strong enough to overcome the repulsive interactions between the fermions. With the great success of the BCS theory, it was not long before the notion of Cooper pairing "tunnelled its way" into other fields of physics. This included the role of Cooper pairs in nuclear structure, the pairing of nucleons in nuclear matter via the exchange of pions and other bosonic particles, which is important in nuclear astrophysics, and the proposal for color superconductivity in a quark gluon plasma, to name a few.
What binds the Cooper phenomena together in these different fields is that the dominant mechanism for pairing of the fermions is the exchange of some bosonic particle that coexists along side the fermions, like the electrons in an elastic medium or the gluons in the quark-gluon soup. It is here that heavy-fermion superconductivity parts company from the standard model for Cooper pairing.

Heavy-fermion superconductors were the first electronic example of Cooper pairs being formed predominantly from the exchange of collective excitations of the many-body medium; liquid $^3$He is the charge neutral superfluid example. In a many-body system, bosonic excitations are formed from collective excitations of the fermions, like density and spin-density fluctuations. Two fermions can interact by the exchange of these bosons. This effective interaction between the fermions can give rise to either repulsive interactions or attractive interactions that form Cooper pairs. This, in general, is an intractable many-body problem because the Cooper pairs will be formed by excitations made up from the same fermions that would like to form other kinds of collective pairs in addition to the Cooper pairs. What made the heavy-fermion problem, as well as liquid $^3$He, special was the separation of the high-energy electronic scales from the low-energy collective scales, which made it possible to develop microscopic and phenomenological theories of the interacting system. This large separation of energy scales is also responsible for the unconventional nature of the superconductivity. The underlying force between the electrons is the strong short-range repulsive coulomb interaction between the electrons in a relative s-wave state. Thus, it is no surprise that s-wave superconductivity is not seen in heavy-fermion superconductors. The unconventional nature of the superconducting state in heavy-fermion superconductors is the Cooper pair trying to find a state that maximizes the attractive interactions while minimizing the strong coulomb repulsion.

There is no other example in condensed-matter physics where the interaction between theory and experiment played such a crucial role in uncovering the unconventional nature of the pairing and the many-body origins of the pairing interaction. Even today, with all of the attention paid to it, there is far less theoretical insight into the physics of the high-temperature superconductor problem than we have in the heavy-fermion problem. Heavy-fermion superconductivity still remains as the model problem for how to do physics in strongly interacting many-body systems.

The field remains healthy, and young scientists still have the hope of exciting new superconductors. The evidence is in last section on the first plutonium-containing superconductor that was discovered recently, and it had the highest transition temperature of any heavy-fermion superconductor. This was absolutely unexpected. There is still much experimental and theoretical work to be done before this subfield matures.
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