Journal of Alloys and Compounds, 213/214 (1994) 232–237
JALCOM 4001

Muon spin relaxation studies of the interplay between magnetism and superconductivity in heavy fermion systems

Robert H. Heffner
Materials Division, MS K764, Los Alamos National Laboratory, Los Alamos, NM 87545 (USA)

Abstract

The interplay between magnetism and superconductivity in heavy fermion systems is discussed and the role of muon spin relaxation in elucidating these properties is emphasized. Relevant properties of all six heavy fermion superconductors are briefly surveyed and instances where superconductivity and magnetism compete, coexist and couple with one another are pointed out. Current theoretical concepts underlying these phenomena are highlighted.

1. Introduction

Because new classes of superconducting materials have been discovered in recent years, the study of superconductivity, only ten years ago thought to be passé, remains a most fascinating challenge for material's researchers. For example, the collection of new superconducting materials now includes the high temperature oxide superconductors, with transition temperatures T_c as high as 130 K, doped C_{60} fullerenes ($T_c \approx 30$ K), low-dimensional organic superconductors ($T_c \approx 10$ K), and heavy fermion (HF) superconductors ($T_c \approx 1$ K). All of these materials exhibit very interesting magnetic phenomena as well. This paper is concerned with a brief discussion of the interplay between magnetism and superconductivity in the HF materials and the role muon spin rotation (μSR) experiments have played in elucidating their properties. Heavy fermion materials involve rare earth (Ce and Yb, usually) and uranium-based compounds in which the f electrons are strongly hybridized with the conduction electrons at low temperatures [1, 2]. In order to understand the superconducting properties of HFs, it is first necessary to have a framework to describe the normal state produced by this strong hybridization.

One of the key normal-state properties of HF materials is that at low temperatures the f electron moments are reduced to a fraction of their high temperature values, which are close to the full f shell moment (about 3 μ_B). This moment compensation occurs through an antiferromagnetic exchange interaction which produces a virtual bound state between the conduction electrons and the f moments. For dilute magnetic ions in metals this is the well known single-ion Kondo interaction. Although this cross-over from full-moment to reduced-moment behavior does not occur through a sharp phase transition, it can still be characterized by a scaling temperature T^*, the coherence temperature. "Coherence" is implied because below T^* the resistivity drops significantly, indicating the loss of inelastic scattering and the formation of the HF state, consisting of renormalized (heavy mass) quasi-particles describable in a Fermi liquid theory by a large linear specific heat coefficient γ. For HF materials $T^* \approx 10$–100 K. Although this general picture is now well accepted, no complete microscopic theory of this many-body state has yet been formulated [1, 2]. The evolution of such a theory is a major challenge for the theory of electrons in materials.

A variety of different low temperature ground states emerges from this background of moment compensation: semiconducting, paramagnetic (PM), antiferromagnetic (AFM) and superconducting. Where magnetic or superconducting phase transitions are found it is clear from the entropy balance that the heavy quasi-particles themselves form the ordered state. In the case of AFM the ordered moments are typically very small ((0.01–0.1) μ_B), as expected from screening by the conduction electrons. Whether the system will exhibit an AFM or PM state depends on a competition between the local on-site exchange interaction, which compensates the local f moment, and the non-local long-range f–f interaction, which gives rise to magnetic order through the Ruderman–Kittel–Kasuya–Yoshida interaction. The intra- and intersite interactions are related through a common conduction electron local moment exchange coupling.

Superconductivity in HF systems is interesting and important because most evidence indicates that both the symmetry of the superconducting order parameter

0925-8388/94/$07.00
SSDI 0925-8388(93)04001-7

and the pairing interaction itself are different from those of more conventional superconductors such as Al or Pb. In conventional superconductors the superconducting gap exists over the entire Fermi surface, and the electrons pair in a zero angular momentum, spin-singlet state which is produced by the electron–phonon interaction. A non-vanishing gap gives rise to exponential temperature dependences for all measurements involving the thermal excitation of quasiparticles across the gap: specific heat, magnetic field penetration depth and nuclear spin–lattice relaxation rate, as examples. However, measurements of these quantities in HF superconductors all exhibit power law temperature dependences, usually considered as evidence for nodes in the energy gap [1].

Power law temperature dependences do not provide definitive evidence for an unconventional gap structure, however [3]. (A conventional gapless superconductor can also exhibit power law behavior, for example). More decisive conclusions can only be drawn from tests of the symmetry-breaking nature of the order parameter $\Delta(k)$. In conventional superconductors $\Delta(k)$ obeys the symmetry of the hamiltonian, which includes rotational, reflection (parity) and time-reversal symmetry. An unconventional superconductor has a lower symmetry in at least one of these respects. Experimental tests of this property include a transition from one superconducting state to another, observation of magnetism associated with the superconducting order parameter, or anisotropy in the temperature dependence of the penetration depth or the critical fields.

2. Experiments

The known HF superconductors are listed in Table 1, together with some properties which are relevant to this discussion. A thorough survey can be found in ref. 2. The manifestations of the interplay between magnetism and superconductivity display much variety in HF systems. This is doubtless because the f electrons themselves are involved in both phenomena and, as discussed below, there is growing evidence that magnetic spin fluctuations (paramagnons) may also be the dominant superconducting pairing mechanism. This is in contradistinction to an earlier class of "magnetic superconductors," the rare earth rhodium borides and molysulfides [4], where the magnetism is localized on the rare earths but the superconductivity is carried by separate conduction electrons which interact weakly with the local moments. In this sense the Cr–Re systems [5] may be more analogous to HF superconductors.

TABLE 1. Heavy fermion superconductors

Material	Structure	γ (J mol^{-1} K^{-2})	T_c (K)	T_N (K)	Moment (μ_B)
$CeCu_2Si_2$	Tetragonal	1.100	0.70	0.8–1.3	0.1
URu_2Si_2	Tetragonal	0.180	1.20	17.5	0.04
UPd_2Al_3	Hexagonal	0.150	2.00	14.5	0.85
UNi_2Al_3	Hexagonal	0.120	1.00	4.4	0.12
UPt_3[a]	Hexagonal	0.450	0.55	5.0	0.03
UBe_{13}[b]	Cubic	1.100	0.90	–	–

[a] Transition at about 0.50 K with very small moment (about 0.001 μ_B).
[b] (U,Th)Be_{13} exhibits transition below 0.48 K with small moment (about 0.01 μ_B).

It is clear from Table 1 that magnetism occurs both above and below the superconducting transition temperature. Below examples are given where these two phases can compete, coexist and/or couple with one another.

2.1. Competition: $CeCu_2Si_2$

This was the first HF superconductor to be discovered and remains the only rare-earth-based system. Extensive studies have shown that the existence of superconductivity and/or magnetism in this system is very sensitive to subtle changes in unit cell volume, which can be induced by La doping and Cu deficit ($\Delta V/V > 0$) or Cu excess and hydrostatic pressure ($\Delta V/V < 0$) [2]. Samples with large unit cell volume tend to be magnetic and non-superconducting, reflecting a reduction in T^*; when the volume is reduced superconductivity appears and T^* is raised. AFM can also be induced by the application of fields in superconducting samples; the field–temperature phase diagram continues to be investigated [6]. In addition, spontaneous magnetism, possibly of spin-glass-like origin, exists together with superconductivity in zero field [7].

Experiments [7, 8] using μSR provide insight into this appearance of both magnetism and superconductivity. In zero field the μSR relaxation function for $CeCu_{2.05}Si_2$ exhibits two components below about 1.35 K, one of which is attributable to paramagnetic domains, with volume fraction A_1, and the other to magnetic domains, with volume fraction A_2 ($A_1+A_2=1$). The temperature dependence of these amplitudes is shown in Fig. 1. The magnetic volume fraction grows below 1.3 K, reaching a maximum at T_c and then decreasing as the superconductivity develops. Furthermore, experiments in an applied field reveal a change in the muon precession frequency below T_c (due to the diamagnetism) only in the PM fraction. Thus superconductivity and magnetism do not appear to coexist in the same sample volume, but instead compete for volume with one another. This competition between magnetism and superconductivity is different from the HF behavior found in the materials discussed below.

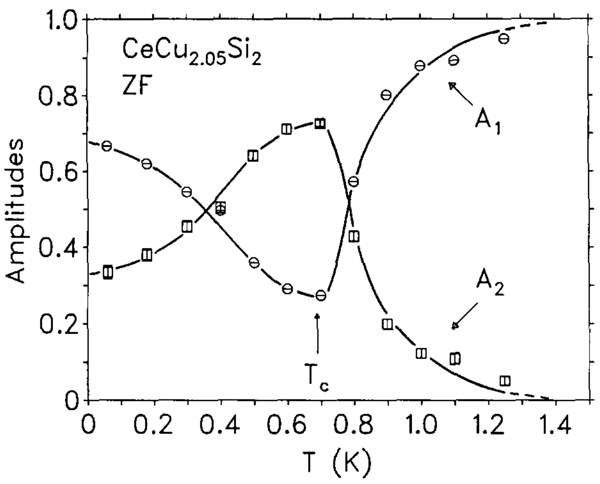

Fig. 1. Temperature dependence of the amplitudes for the two observed components of the zero-field μSR relaxation function in $CeCu_{2.05}Si_2$ [8]. A_1 is the paramagnetic component and A_2 is the magnetic component. The arrow marks the superconducting transition temperature T_c.

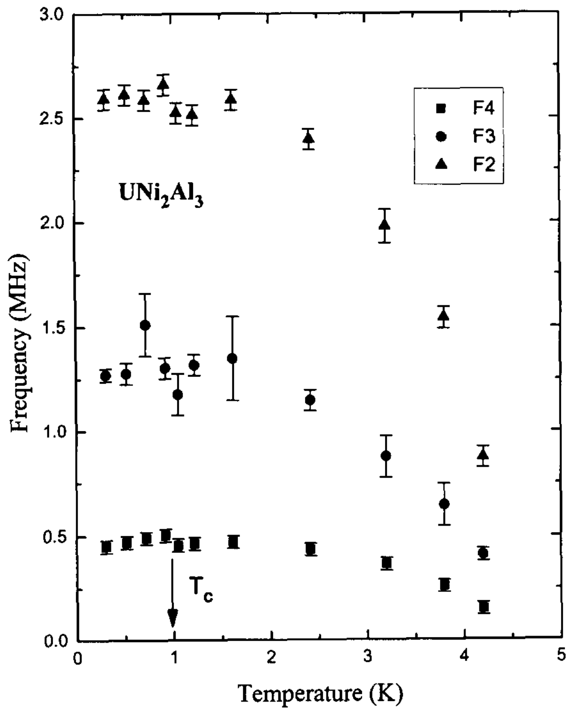

Fig. 2. Temperature dependence of the three observed precession frequencies in zero applied field for UNi_2Al_3 [8, 10]. The arrow marks the superconducting transition temperature T_c.

2.2. Coexistence: UNi_2Al_3, UPd_2Al_3, URu_2Si_2

These three actinide superconductors all exhibit magnetic order above T_c which coexists with superconductivity below T_c. A plot of the muon precession frequency *vs*. temperature in UNi_2Al_3 is shown in Fig. 2 for zero applied field [9]. The muon frequency spectrum exhibits four components: three precession signals (Fig. 2) and one non-precession signal, possibly corresponding to different interstitial muon stopping sites. The dipole field at each muon site depends on the AFM structure and the magnitude of the local moment μ. The data are consistent with $\mu \approx 0.1\ \mu_B$. A most important point for this discussion is that the muon precession frequencies and their amplitudes are unaltered by the onset of superconductivity, indicating not only a coexistence but also a weak interaction between the two types of ground states.

A similar situation is found in UPd_2Al_3 [11]. Neutron scattering experiments [12] reveal a moment $\mu \approx 0.85\ \mu_B$, ordered ferromagnetically in the basal plane and antiferromagnetically along the c axis below 14.5 K. Several different magnetic phases have been found in the field–temperature phase diagram [11]. The μSR data [8, 13] reveal only one relaxation component, unlike UNi_2Al_3. This component corresponds to a single occupancy site for the muon, that of highest symmetry where the dipole fields from the AFM order cancel, and so no precession signals are seen. This same site is associated with the non-precessing component in isostructural UNi_2Al_3.

The temperature dependence of the transverse field μSR rate in polycrystalline UPd_2Al_3 is shown in Fig. 3 [8, 13]. This rate increases at T_N and again at T_c, below which the local-field distribution increases owing to the flux lattice produced in the mixed state of the superconductor. Note that the line broadening from the AFM state persists below T_c, again indicating coexistence with superconductivity.

A similar situation is seen in a single crystal of URu_2Si_2, another HF superconductor with $T_c = 1.3$ K and $T_N = 17$ K. Here the much-reduced moments ($\mu \approx 0.04\ \mu_B$) are ordered antiferromagnetically along the c axis [14]. The μSR rate [15] for a field applied parallel to the c axis exhibits an increasing linewidth as the temperature is decreased below T_N. Below T_c

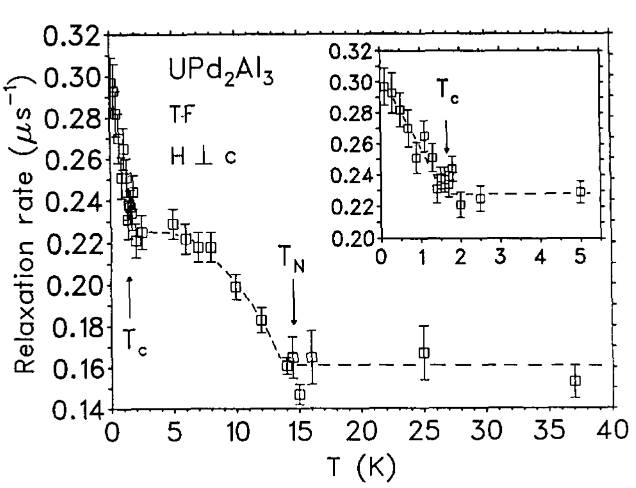

Fig. 3. Temperature dependence of the 5 kOe transverse field μSR relaxation rate in UPd_2Al_3 [8, 13].

the relaxation rate increases and the precession frequency changes, both reflections of entering the superconducting state, similar to the case of UPd_2Al_3. Again only a single relaxation component is seen.

It is important to note that in these three HF superconductors the muon data show that the magnetism and superconductivity coexist on a microscopic scale; that is, there is not one relaxation component which displays magnetic behavior and another which responds to superconductivity, as in $CeCu_2Si_2$. The μSR data also show that, although the magnetism and superconductivity in UNi_2Al_3, UPd_2Al_3 and URu_2Si_2 coexist throughout the entire sample volume, they do not appear to interact strongly, despite the fact that the f electrons are involved in both ground states. This is also different from $CeCu_2Si_2$ discussed above.

2.3. Coupling: UPt_3 and $(U,Th)Be_{13}$

The examples given above all have AFM transition temperatures greater than T_c. This also occurs in UPt_3, where a magnetic transition at 5 K was first discovered by μSR [16]. Comprehensive neutron scattering experiments [17] then delineated the magnetic structure, which consists of small moments ($\mu \approx 0.03\ \mu_B$) antiferromagnetically ordered in the basal plane. Most important, however, is that in zero applied field the growth of the magnetic Bragg intensity for decreasing temperatures below T_N is reversed and falls again below T_c. The specifics of this behavior are both field and temperature dependent [17]. This reflects a clear interaction between the superconducting and magnetic order parameters not found in the superconductors mentioned above.

Subsequent studies using a variety of probes have revealed a rich phase diagram in the field–temperature planes for UPt_3, in which at least three different superconducting phases have been discovered [18]. In zero field and ambient pressure there are two superconducting transitions, an upper phase near $T=0.55$ K, and a lower phase near $T=0.48$ K. There is evidence [19] that this splitting is produced by the coupling between the AFM order parameter (setting in at 5 K) and the superconducting order parameter. Remarkably, recent zero-field μSR experiments reveal the onset of additional very weak spontaneous magnetism below the lower of the two superconducting transition temperatures [20]. These issues will be discussed again below.

UBe_{13} itself exhibits no magnetic order down to 10 mK, only a superconducting transition at $T_{c1}=0.9$ K. However, when UBe_{13} is doped with Th the superconducting transition temperature exhibits a non-monotonic suppression [21], as shown in Fig. 4. Furthermore, for $0.019<x<0.043$ in $U_{1-x}Th_xBe_{13}$, a second phase transition [22] occurs at T_{c2} below T_{c1}. μSR experiments [23] reveal the onset of magnetism below T_{c2}, again

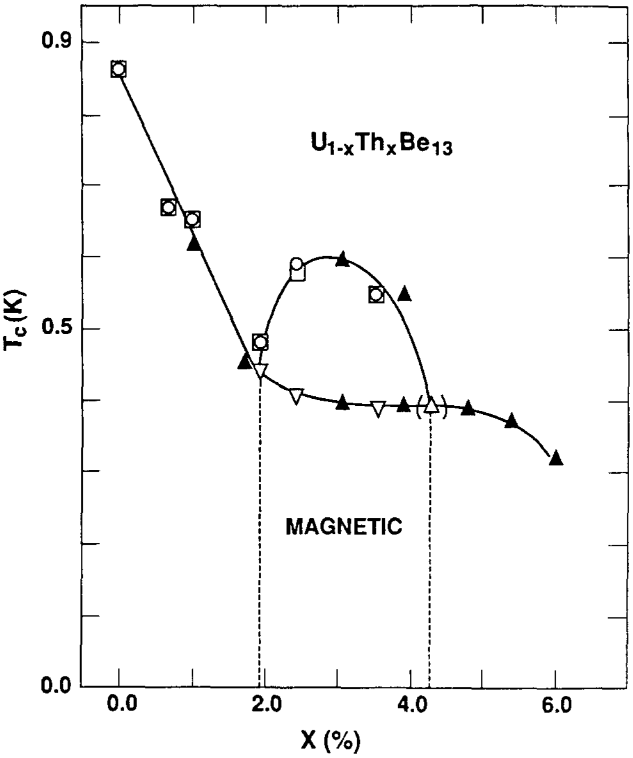

Fig. 4. The superconducting transition temperature T_c as a function of Th concentration x in $U_{1-x}Th_xBe_{13}$ [23]. The symbols are explained in ref. 23. Small-moment magnetism appears in the region marked "magnetic".

with very small moments ($\mu \leqslant 0.01\ \mu_B$). The large specific heat jump at T_{c2} indicates a change in the superconducting state below this temperature. What is remarkable is that the magnetic phase boundary at T_{c2} begins and terminates on the superconducting phase boundary at T_{c1} [23]. This is similar to the case of UPt_3, and again suggests possible coupling of the magnetic and superconducting order parameters. Finally, we note that the normal state of UBe_{13} has a resistance peak [24] at about 2.2 K which moves lower in temperature as Th is added, so that it intersects the superconducting phase boundary T_{c1} at $x \approx 0.019$, just where the suppression of T_{c1} is reversed (see Fig. 4). Recent magnetoresistance and specific heat studies of $(U,Th)Be_{13}$ are consistent with associating the resistance anomaly with correlated spin fluctuations in the heavy electron system [25]. These spin fluctuations may be freezing out below T_{c2} giving rise to a small-moment AFM state which couples to the superconducting order parameter as in UPt_3.

3. Concluding discussion

The above examples show that the interplay of magnetism and superconductivity has great variety in HF materials. At this point there is no detailed microscopic theory which can uniquely explain all of these phenomena [26]. Nevertheless, there is a line of reasoning which explains some of the phenomena and provides a framework for thinking about HF superconductors. An important point is that the strongly hybridized f electron quasi-particles are involved in the magnetic and superconducting phase transitions in these systems. Second, because these quasi-particles exhibit strong AFM correlations even in the PM state, it is tempting to consider that AFM spin fluctuations may also provide the dominant superconducting pairing force in HF materials. This assumption is strengthened by theoretical studies [27] which show that AFM paramagnons can give rise to both a spin-density-wave (SDW) instability and an even-parity, anisotropic pairing state (d wave) for strong on-site Coulomb repulsion. Likewise ferromagnetic paramagnons favor triplet p wave pairing [27]. A conventional isotropic pairing state is not indicated; indeed, spin fluctuations are pairbreaking for s wave pairing [28]. This is consistent with most all of the data for HF superconductors, which point to an unconventional order parameter with nodes on the Fermi surface. These data include the power law temperature dependences for low temperature transport and thermodynamic measurements mentioned above and the evidence for multiple superconducting phases and anisotropic critical fields in some materials. Thus the f electron Fermi surface could be divided between superconductivity and AFM in such a way that the SDW nesting occurs where there are nodes in the anisotropic superconducting order parameter [29]. This sharing of the Fermi surface seems to be the case in URu_2Si_2, for example, where the specific heat jumps at T_N and T_c indicate that neither phase transition occupies the full Fermi surface by itself [30]. Such a picture provides a natural way of understanding how superconductivity and AFM can coexist in these systems.

Interactions between superconductivity and magnetism can be described through explicit terms in the free energy which couple the tensors representing the magnetization and the superconductivity, while preserving the overall symmetry. In UPt_3, for example, the magnetization below 5 K lies in the basal plane [17]. One model [26] for the superconducting order parameter in UPt_3 assumes a complex two-dimensional vector with basal plane components (η_x, η_y), which can therefore couple through a vector product to the magnetization. Within the model this coupling causes the zero-field splitting of the superconducting phase transitions near 0.55 K. If a superconducting order parameter of similar symmetry were present in URu_2Si_2, however, no coupling with the magnetization in that system would occur because the moments are polarized along the c axis. This could account for the observed constancy of the magnetization below T_c in URu_2Si_2.

These ideas, only briefly mentioned here, have been discussed in detail in the recent literature [1, 2, 3, 26]. While such concepts are useful, they are not definitive. Although HF superconductors exhibit many common properties which these concepts encompass, the distinguishing normal- and superconducting-state characteristics of each material, such as band properties, and coherence and scattering lengths, must be examined before the interplay between magnetism and superconductivity in that material can be understood. For example, the absence of microscopic coexistence in $CeCu_2Si_2$ may reflect a fundamental difference between 4f and 5f systems (such as the degree of hybridization), as may the fact that only one Ce-based HF superconductor has been discovered. Alternatively, recent band structure calculations for this system suggest that magnetic phase transitions can be induced within a heavy quasi-particle band by magnetic fields or small changes in the band filling [31].

One final point must be mentioned regarding the very weak magnetism which sets in below T_c in UPt_3 and $(U,Th)Be_{13}$. The above discussion implies that these magnetic correlations are induced by a magnetic exchange interaction. It is also possible that the superconducting phase itself may possess orbital [32] or spin [33] magnetism. Such a phase violates time-reversal symmetry and can be expected for an unconventional superconductor (^3He is a good example). This picture would explain why the magnetism occurs right at T_c and is confined to the superconducting phase boundaries. So far these is no definitive evidence which can distinguish between purely magnetic or superconducting origins for these small moments, however.

Acknowledgments

I would like to thank my colleagues A. Amato, W. Beyermann, Z. Fisk, D.E. MacLaughlin, A. Millis, J.A. Mydosh, H.R. Ott, A. Schenck, J.L. Smith and J.D. Thompson for continuing collaborations and helpful comments. This work is supported in part by the US Department of Energy–BES–DMS.

References

1 Z. Fisk, D.W. Hess, C.J. Pethick, D. Pines, J.L. Smith, J.D. Thompson and J.O. Willis, *Science, 239* (1988) 33.
2 N. Grewe and F. Steglich, *Handbook on the Physics and Chemistry of Rare Earths,* Vol. 14, Elsevier, Amsterdam, 1991, p. 343.
3 D. Rainer, *Phys. Scr. T, 23* (1988) 106.
4 K. Machida, *J. Low Temp. Phys., 37* (1979) 583.
5 Y. Nishihara, K. Murata, M. Tokumoto and Y. Yamaguchi, *Jpn. J. Appl. Phys., 26* (Suppl. 26-3) (1987) 1297.

6 B. Wolf, G. Bruls, W. Sun, W. Assumus, B. Luthi, H. Schimanski, K. Gloos and F. Steglich, *Physica B, 186–188* (1993) 279.

7 Y.J. Uemura, W.J. Kossler, X.H. Yu, H.E. Schone, J.R. Kempton, C.E. Stronach, S. Barth, F.N. Gygax, B. Hitti, A. Schenck, C. Baines, W.F. Lankford, Y. Onuki and T. Komatsubara, *Phys. Rev. B, 39* (1989) 4726.

8 A. Amato, *Int. Conf. on Strongly Correlated Electron Systems, La Jolla, CA, August 1993.*

9 A. Amato, C. Geibel, F.N. Gygax, R.H. Heffner, E. Knetsch, D.E. MacLaughlin, C. Schank, A. Schenck, F. Steglich and M. Weber, *Z. Phys. B, 86* (1992) 159.

10 A. Amato, R. Feyerherm, F.N. Gygax, A. Schenck, M. Weber, R. Caspary, P. Hellman, C. Schank, C. Geibel, F. Steglich, D.E. MacLaughlin, E.A. Knetsch and R.H. Heffner, *Europhys. Lett., 19* (1992) 127.

11 C. Geibel, S. Thies, D. Kaczorowski, A. Mehner, A. Grauel, B. Seidel, U. Ahlheim, R. Helfrich, K. Petersen, C.D. Bredl and F. Steglich, *Z. Phys. B, 83* (1991) 305.
C. Geibel, A. Bohm, R. Caspary, K. Gloos, A. Grauel, P. Hellman, R. Modler, C. Schank, G. Weber and F. Steglich, *Physica B, 186–188* (1993) 188.

12 A. Krimmel, P. Fischer, B. Roessli, H. Maletta, C. Geibel, C. Schank, A. Grauel, A. Loidl and F. Steglich, *Z. Phys. B, 86* (1992) 161.

13 R. Feyerherm, A. Amato, C. Geibel, F.N. Gygax, T. Komatsubara, A. Schenck and F. Steglick, *Int. Conf. on Strongly Correlated Electron Systems, La Jolla, CA, August 1993.*

14 T.E. Mason, B.D. Gaulin, J.D. Garrett, Z. Tun, W.J.L. Buyers and E.D. Isaacs, *Phys. Rev. Lett., 65* (1990) 3189.

15 E.A. Knetsch, A.A. Menovsky, G.J. Nieuwenhuys, J.A. Mydosh, A. Amato, R. Feyerherm, F.N. Gygax, A. Schenck, R.H. Heffner and D.E. MacLaughlin, *Physica B, 186–188* (1993) 300.

16 R.H. Heffner, D.W. Cooke and D.E. MacLaughlin, in L.C. Gupta and S.K. Malik (eds.), *Theoretical Aspects of Valence Fluctuations and Heavy Fermions,* Plenum, New York, 1987, p. 319.

17 G. Aeppli, D. Bishop, C. Broholm, E. Bucher, K. Siemensmeyer, M. Steiner and N. Stusser, *Phys. Rev. Lett., 63* (1989) 676.

18 G. Bruls, D. Weber, B. Wolf, P. Thalmeier, B. Luthi, A. de Visser and A. Menovsky, *Phys. Rev. Lett., 65* (1990) 2294.
A. Adenwalla, S.W. Lin, Q.Z. Ran, Z. Zhao, J.B. Ketterson, J.A. Sauls, L. Taillefer, D.G. Hinks, M. Levy and B.K. Sarma, *Phys. Rev. Lett., 65* (1990) 2298.

19 S.M. Hayden, L. Taillefer, C. Vettier and J. Flouquet, *Phys. Rev. B, 46* (1992) 8675.

20 G.M. Luke, A. Keren, L.P. Le, W.D. Wu, Y.J. Uemura, D.A. Bonn, L. Taillefer and J.D. Garrett, *Physica B, 186–188* (1993) 264.

21 H.R. Ott, H. Rudigier, Z. Fisk and J.L. Smith, *Phys. Rev. Lett., 50* (1983) 1595.

22 H.R. Ott, H. Rudigier, Z. Fisk and J.L. Smith, *Phys. Rev. B, 31* (1985) 1651.

23 R.H. Heffner, J.L. Smith, J.O. Willis, P. Birrer, C. Baines, F.N. Gygax, B. Hitti, E. Lippelt, H.R. Ott, A. Schenck, E.A. Knetsch, J.A. Mydosh and D.E. MacLaughlin, *Phys. Rev. Lett., 65* (1990) 2816.

24 H.A. Borges, J.D. Thompson, M.C. Aronson, Z. Fisk and J.L. Smith, *J. Magn. Magn. Mater., 76–77* (1988) 235.

25 E.A. Knetsch, G.J. Nieuwenhuys, J.A. Mydosh, R.H. Heffner and J.L. Smith, to be published.

26 M. Sigrist and K. Ueda, *Rev. Mod. Phys., 63* (1991) 239.

27 D.J. Scalopino, E. Loh, Jr., and J.E. Hirsch, *Phys. Rev. B, 34* (1986) 8190.

28 A.J. Millis, S. Sachdev and C.M. Varma, *Phys. Rev. B, 37* (1988) 4975.

29 M. Kato and K. Machida, *Phys. Rev. B, 37* (1988) 1510.

30 T.T.M. Palstra, A.A. Menovsky, J. van den Berg, A.J. Dirkmaat, P.H. Kes, G.J. Nieuwenhuys and J.A. Mydosh, *Phys. Rev. Lett., 55* (1985) 2727.

31 G. Zwickangl and U. Pulst, *Physica B, 186–188* (1993) 895.

32 G.E. Volovik and L.P. Gor'kov, *Sov. Phys. JETP, 61* (1985) 842.

33 M. Sigrist and T.M. Rice, *Phys. Rev. B, 39* (1989) 2200.