# Magnetism in Heavy-Electron Metals

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## Abstract

Originally it was believed that the presence of heavy-mass charge carriers at low temperatures in some special rare-earth or actinide compounds was simply the result of a suppression of magnetic order in these materials. Various experiments reveal, however, that magnetic order may occur from a heavy-electron state or that a heavy-electron state may also develop within a magnetically ordered matrix. It turned out that pure compounds without any sign of a cooperative phase transition down to very low temperatures are rare but examples are known where microscopic experimental probes give evidence for strong magnetic correlations involving moments of much reduced magnitude ($\leq 0.1\mu_B$) in such cases. It appears that electronic and magnetic inhomogeneities, both in real and reciprocal space occur which are not simply the result of chemical inhomogeneities. Long range magnetic order among strongly reduced magnetic moments seems to be a particular feature of some heavy-electron materials. Other examples show, that disorder may lead to a suppression of cooperative phase transitions and both macroscopic and microscopic physical properties indicate that conservative model calculations are not sufficient to describe the experimental observations. The main difficulty is to find a suitable theoretical approach that considers the various interactions of similar strength on an equal footing. Different examples of these various features are demonstrated and discussed.

## 1 Introduction

The stability of magnetic moments in a metallic environment has been the subject of many theoretical and experimental studies but the ideas considered in the early works of Friedel (1956), Blandin (1958), Anderson (1961) and Kondo (1964) still provide the essential background for discussing recent and new experimental observations. The low temperature behaviour of simple metals is believed to be well understood on the basis of Landau's (1956) Fermi liquid model. The often observed transition to a superconducting state can be well explained by the BCS theory (Bardeen et al., 1957) and a pairing potential that is due to the interaction between conduction electrons and lattice excitations (phonons). Less transparent is the behaviour of $d$- and $f$-electron transition metals and compounds. Particular recent interest is connected with a class of substances for which electron-electron

interactions and correlations are dominating factors, the so called heavy-electron systems. For the description of the properties of these metallic systems, many-body effects can no longer be neglected or treated with simple approximation schemes. Materials that we discuss here contain ions with incompletely occupied atomic $f$-electron orbitals, leading to well defined ionic moments containing both orbital and spin components. These ions occupy regular lattice sites and their moments interact with the ensemble of itinerant charge carriers. In most cases it may be expected that the adopted ground state of these materials is of some magnetically ordered variety, a result of the coupling of these moments via the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction mediated by the conduction electrons (Ruderman and Kittel, 1954 ; Kasuya, 1956; Yosida, 1957). As is well known from the above cited work, a metallic environment may also lead to a partial or complete compensation of a single magnetic moment. Instead of considering the stability of only a single magnetic moment in a metallic environment, the new developments that are considered here necessitate the same treatment for a regular array of magnetic moments in three dimensions. Various new schemes to treat this type of problem have recently been employed (Jones, 1991; Sheng et al., 1994; Keiter et al., 1995; Wölfle, 1995) and, in particular, the possibility of new types of metallic ground states, different from that of a Fermi liquid, has received considerable attention in the last few years (Cox, 1987; Coleman et al., 1994; Ludwig, 1994).

Below we intend to discuss a few experimental observations which indicate that due to competing interactions of similar magnitude, ground states that are more complex than previously envisaged may be adopted. The main purpose of this presentation and discussion is to provide experimental evidence for the new aspects that were mentioned above, but this short review is certainly not exhaustive. The selected series of examples, however, may serve as a guideline for future explorations in this field, both experimentally and hopefully also theoretically.

## 2 Magnetic inhomogeneities in real space

A well documented case for this type of feature has been established for the compound $CeAl_3$. This compound has for a long time been considered as a standard example for which well defined localized magnetic moments at low temperatures donate their degrees of freedom to a new kind of state whose properties are characteristic for a Fermi liquid with strongly renormalized parameters and is formed by quasiparticles with considerably enhanced effective masses. This view was based on the results of experiments probing thermal- and transport properties at high and low temperatures, i.e., between 0.05 and 300 K (Andres et al., 1975; Ott et al., 1984a).

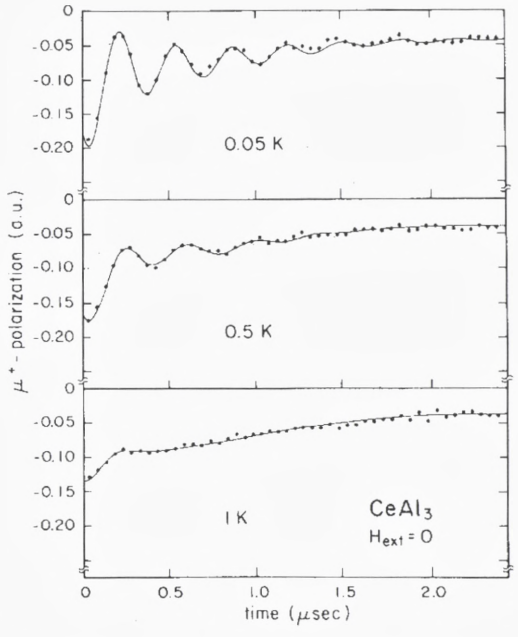


Figure 1. Time dependence of the zero-field $\mu^+$ polarization in $CeAl_3$ at low temperatures. The solid lines are fits to the data (see Barth et al., 1989).

Subsequent microscopic studies involving $\mu$SR and NMR experiments revealed a more complicated situation, however. At very low temperatures and in zero magnetic field an oscillatory component in the $\mu$SR spectra shown in Fig. 1 indicated the presence of at least quasistatic magnetic correlations inducing a corresponding local field at the muon site (Barth et al., 1987). The temperature dependence of the oscillation frequency in the range of observation between 0.05 and 0.7 K is rather weak and above this temperature the oscillatory component is no longer discernible. The observation of a single frequency proves that all the muons experiencing the corresponding local field, which doesn't vary much with temperature, are trapped and decay on equivalent sites. The temperature dependence of the $\mu^+$-decay asymmetry indicates that the number of trapping sites exposed to the quasistatic magnetic field increases with decreasing temperature. As $T$ approaches 0, a large part of the sample is magnetically correlated (Barth et al., 1989). The growth of the correlated regions occurs without any manifestation of a cooperative phase transition, compatible with all observations when probing macroscopic properties.

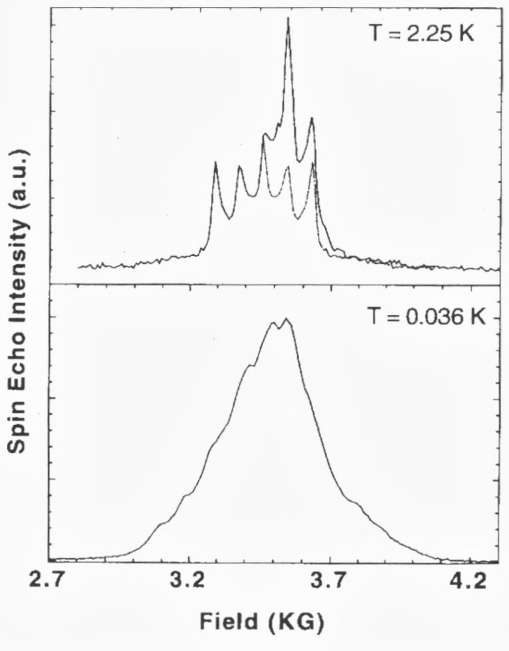


Figure 2. Low frequency NMR spectra of $CeAl_3$ at low temperatures. The dotted line indicates the quadrupolar split spectrum of the oriented part of the powder sample.

Additional $\mu$SR experiments in non-zero magnetic fields were intended to identify with some reliability the $\mu^+$-decay site in the crystal lattice. Accompanying simulation calculations and a thorough analysis of all the available data indicate a magnetic moment of only 0.05 $\mu_B$ residing on the $Ce^{3+}$ ions within the correlated regions below 0.7 K (Schenck, 1993). It seems obvious that both the small value of the moments involved in the correlated regions and the unusual, spatially inhomogeneous increase of magnetically correlated volume with decreasing temperature deserved more attention. Subsequent low-field NMR experiments (Gavilano et al., 1995a) on the same material and at temperatures between 0.04 and 20 K to a large extent confirmed the previous microscopic observations. Above 3 K, sharp and quadrupole-split resonance lines of $^{27}Al$ nuclei reveal a normal paramagnetic environment. Below 3 K, however, a broad background intensity in these spectra grows with decreasing temperature and at the lowest temperatures the NMR spectrum consists of a broad and only faintly structured peak with a width of a few hundred gauss (see Fig. 2). The growing background intensity may be interpreted as being

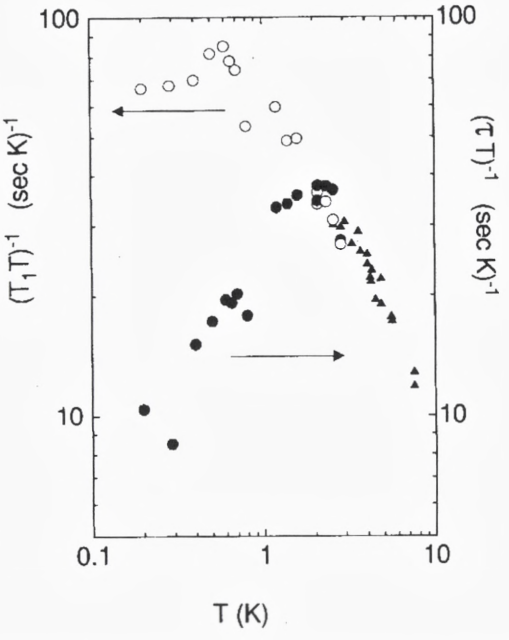


Figure 3. Temperature dependence of the NMR relaxation rates related to the two different parts of the spectra of $CeAl_3$.

due to an increase of the number of nuclei which are exposed to an internal field barely changing with temperature and of the order of 500 gauss. Considering this field value and the geometrical arrangement of Ce and Al atoms in the hexagonal crystal structure of $CeAl_3$, again an average moment of the order of 0.05 $\mu_B$/Ce ion may be deduced. The broadening of the quadrupole split lines of nuclei in a paramagnetic environment is thought to arise from the fact that the correlated regions are dispersed and rather small in volume, thereby allowing a large number of the nuclei in the paramagnetic parts of the sample to be close to a boundary between a correlated and a paramagnetic region.

Measurements of the spin–lattice relaxation time $T_1$ revealed that the coupling of the nuclear magnetisation to its environment is quite different for either the correlated or the paramagnetic regions (see Fig. 3). Above 3 K, the relaxation occurs via a single channel characterized by a single value for $T_1$ which increases considerably with decreasing temperature. Below 3 K, two different relaxation rates may be distinguished. The rate related with the paramagnetic regions increases further with decreasing temperature and finally, below 0.7 K, the product $(T_1T)^{-1}$

saturates at a much enhanced value of 65 $K^{-1}$. For pure Al, this value is 0.56 $K^{-1}$. The temperature dependence of the relaxation rate associated with the correlated regions is completely different and the corresponding values of $(T_1T)^{-1}$ decrease considerably with temperature. At the lowest temperatures of observation the difference in these relaxation rates is about one order of magnitude.

All these microscopic observations indicate that the low temperature state of $CeAl_3$ cannot simply be identified as a strongly renormalized Fermi liquid state. There is strong evidence for the coexistence of two magnetically and electronically inequivalent phases at very low temperatures. Although in retrospect some of the features of thermal properties (specific heat, magnetic susceptibility) below 1 K might be considered as indicative for the behaviour described above, the transport properties certainly reveal no such manifestation. Additional recent experiments on small single crystals (Lapertot et al., 1993) and material with small amounts of non magnetic impurities on the Ce sites (Andraka et al., 1995) confirm that the ground state of $CeAl_3$ is very close to being magnetically ordered.

## 3 Electronic inhomogeneities in momentum space

As we pointed out in the introduction, long range magnetic order in metals is very often the result of the RKKY interaction, a coupling of magnetic moments mediated by conduction electrons. The oscillatory nature of this interaction is a result of the Fermi–Dirac type of occupation probability of the electronic states in $k$-space and we intend to demonstrate that different parts of the Fermi surface may be involved in quite different ways in the formation of the ground state of a metal. As an example we choose the case of $UCu_5$.

Experimental studies of the low temperature properties of this compound gave the first evidence that a heavy-electron state may also develop in the environment of a magnetically ordered matrix (Ott et al.,1985), a feature that was not anticipated in early discussions concerning the formation of massive states of itinerant electrons. Various macroscopic and microscopic measurements established the rather conventional antiferromagnetic order that develops among the U magnetic moments of the order of 1 $\mu_B$/U ion in $UCu_5$ below 15 K (van Daal et al., 1975; Murasik et al., 1974; Schenck et al., 1990). The phase transition is clearly manifested by anomalies in the temperature dependence of the specific heat $C_p(T)$ and the electrical resistivity $\rho(T)$. The feature of this latter anomaly implies that the phase transition induces a partial gapping of the Fermi surface thereby reducing the amount of available itinerant charge carriers (Bernasconi et al., 1994). The formation of this gap has more recently been confirmed by measurements of the optical reflectivity, indicating that the transition is at least partially due to

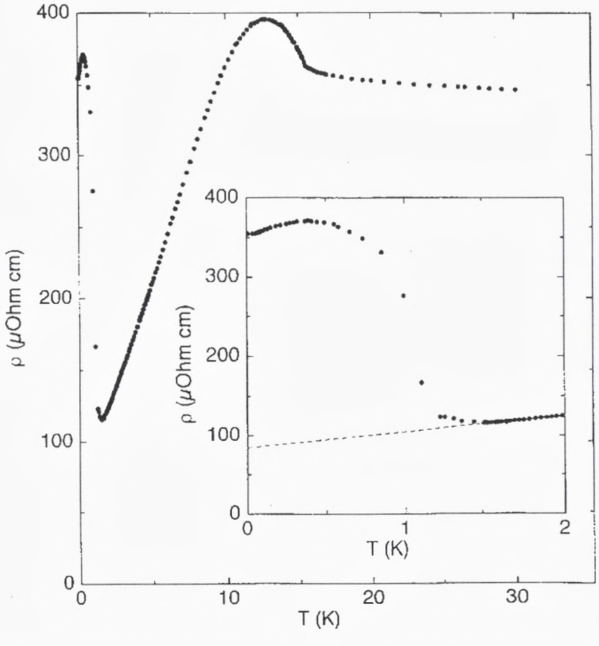


Figure 4. Temperature dependence $\rho(T)$ of the electrical resistivity of $UCu_5$ between 0.02 and 30 K. The inset emphasizes $\rho(T)$ below 2 K.

a magnetic Fermi surface instability (Degiorgi et al., 1994). The temperature dependence of $\rho$ between 0.03 and 30 K is shown in Fig. 4. It may be seen that the remaining free carriers experience a drastic reduction in scattering below about 12 K, most likely due to the combined effect of less magnetic scattering and the onset of coherence due to electronic correlation effects with decreasing temperature.

These correlation effects lead to a distinct increase of the $C_p(T)$ ratio with decreasing temperature below 4 K, reaching a value exceeding 300 mJ/mole$K^2$ below 2 K (Ott et al., 1985). The correlated electron system now by itself loses its stability and another cooperative phase transition at approximately 1 K is indicated by, again, anomalies in $C_p(T)$, shown in Fig. 5, and $\rho(T)$ (see Fig. 4). Below 1 K, $\rho(T)$ reaches a maximum at 0.4 K and subsequently decreases somewhat as $T$ approaches 0. The anomaly of $C_p(T)$ is small but distinct, the corresponding entropy change is negligible compared to $R \ln 2$. Below 0.7 K, $C_p$ decreases linearly with temperature to zero and the ratio $\gamma = C_p/T$ is 80 mJ/mole$K^2$. Both these observations are again compatible with a sizeable reduction of occupied electronic states at the Fermi energy induced by the 1 K transition. Additional transport

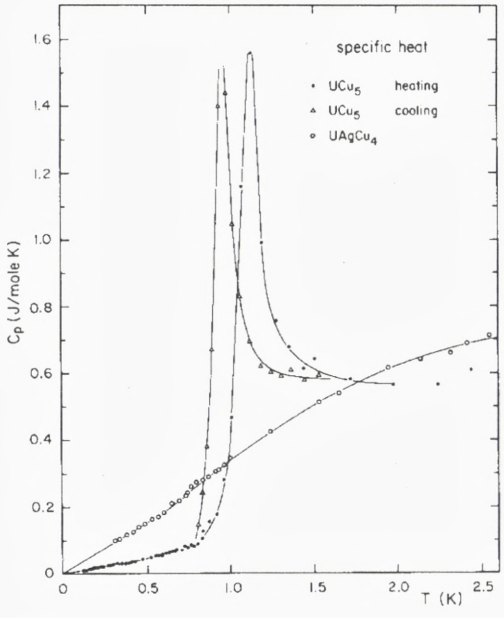


Figure 5. Specific heat of $UCu_5$ and $UAgCu_4$ between 0.1 and 2.5 K.

experiments (Bernasconi et al., 1994) and spectroscopic measurements (Nakamura et al., 1991) support the conclusion that the remaining itinerant charge carriers form a state with the features of a renormalized Fermi liquid. This state, however, coexists with an antiferromagnetically ordered state which is partly due to a spin-wave-type instability and yet another ordered state developing below 1 K whose order parameter has not been established yet.

This coexistence is indicated because the 1 K transition in zero magnetic field has very little influence on the ordered state that has been established to form below 15 K. At the 1 K transition the magnetic susceptibility shows only a minute increase with decreasing temperature (Chernikov et al., 1995). The microscopic probing of the magnetism of $UCu_5$ invoking $\mu$SR and neutron scattering experiments (Schenck et al., 1990) revealed that within experimental resolution no change of the ordered structure nor in the magnitude or orientation of the ordered moments can be inferred. The only noticeable manifestation of this transition in $\mu$SR or neutron scattering data is an increase in the relaxation rate inferred from $\mu^+$-decay spectra. An example for one of the decay channels is shown in Fig. 6. A possible implication of this result could be the formation of some order among tiny

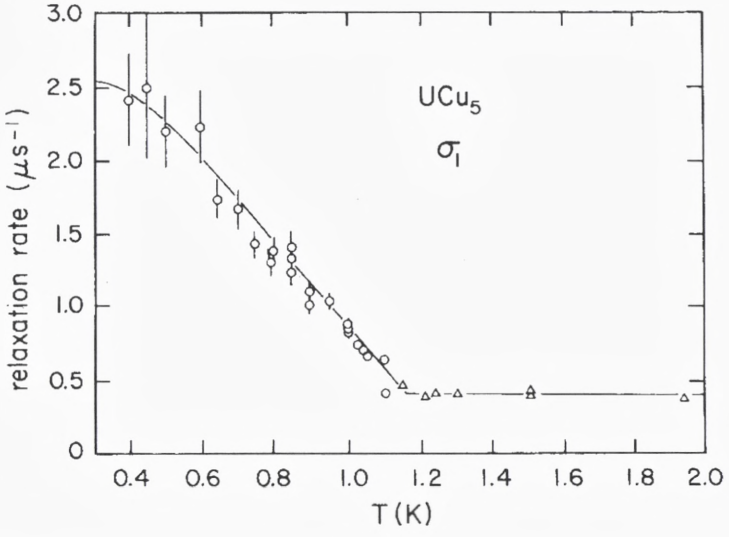


Figure 6. Temperature dependence of the $\mu$SR relaxation rate in one of the decay channels of $UCu_5$ below 2 K.

moments, not detectable by neutron scattering, again due to a Fermi surface instability involving states with enhanced effective masses. The estimated magnitude of such moments from $\mu$SR data is definitely less than 0.01 $\mu_B$. Other conjectures such as the formation of a small internal distortion of the crystal lattice or the transition from a multi-$q$ to a single-$q$ state of magnetic order (Nakamura et al., 1994; Lopez de la Torre et al., 1995) seem incompatible with the combined data of both macroscopic and microscopic experiments. The 1 K transition is extremely sensitive to impurities and imperfections in general (Ott et al., 1989), a feature that is often observed for heavy-electron systems, particularly also in connection with superconducting transitions in such materials and the formation of a correlated state, as in this case (Ott et al., 1987). For some deliberately introduced impurities, especially those which occupy Cu sites, also the 15 K transition is considerably affected, in not the same excessive way, however (Ott et al., 1989).

The main question of how this subdivision of the electronic subsystem has to be addressed theoretically is not easily answered. Estimates based on band structure calculations reproduce both the Néel temperature of 15 K and the magnitude of the ordered moment of the antiferromagnetic order quite well (Norman et al.,1988). Any description of the features at very low temperatures, however, are clearly beyond the capacity of such approaches. Considering the crystal structure of $UCu_5$

it may be noted that cation and anion sites are well separated and this may lead to an intrinsic anisotropy of possible interactions which are all, judging from the experimental observations, rather small and not very different in magnitude. Most importantly, the fact that a heavy-electron state may also form even within a lattice of antiferromagnetically aligned $f$-electron moments seems of some significance in view of theoretical models describing corresponding correlated systems.

More recently it has been speculated that the low-temperature properties of alloys of the form $UCu_{5-x}Pd_x$ with $x \sim 1$ indicate a non Fermi liquid type behaviour, both from macroscopic and microscopic investigations (Andraka et al., 1993; Maple et al., 1995; Bernal et al., 1996). Recent optical measurements (Degiorgi et al., 1996) confirm that at low temperatures $T$ and for low frequencies $\omega$, the charge transport relaxation rate varies almost linearly with $T$ and $\omega$, and not with $T^2$ and $\omega^2$, the expected functional dependencies claimed for a Fermi liquid.

# 4 Magnetic ordering in the presence of heavy electrons

The possibility of magnetic order in the presence of heavy electrons may be demonstrated very well by discussing the low temperature properties of the compound $U_2Zn_{17}$. In Fig. 7 we show results of the electronic part of the low-temperature specific heat of $U_2Zn_{17}$ which was obtained by subtracting from the total specific heat the lattice contribution as evaluated from corresponding measurements on the isostructural compound $Th_2Zn_{17}$ (Ott et al., 1984b). The very large $C_p^{el}/T$ ratio of 550 mJ/mole K$^2$ indicates the anomalously enhanced electronic specific heat above $T_N$. As evidenced by the discontinuous change of $C_p/T$ around 9.7 K the phase transition is very sharp. The electronic part of the specific heat below 5 K can very well be approximated by $C_p^{el} = \gamma T + \beta T^3$ where the prefactor of the linear term is about 1/3 of the $C_p^{el}/T$ ratio above $T_N$. Since recent optical experiments (Degiorgi et al., 1994) have shown that this reduction cannot be traced back to the formation of a partial gap at the Fermi surface, a reduction of the effective mass of the charge carriers induced by the onset of magnetic order seems to be the cause for this observation. The second term is typical for a contribution due to magnetic excitations in the ordered state. The solid line in Fig. 7 indicates that a BCS type curve, taking into account the remaining electronic specific heat below $T_N$, does not describe the experimental results. In view of the absence of a gap formation in the electronic spectrum this may not be too surprising. In connection with this phase transition we also note that the entropy loss due to the transition is anomalously small, i.e. much less than $2R \ln 2 = 11.52$ J/mole K, the entropy that would be released by lifting the degeneracy of a doubly degenerate ground state of

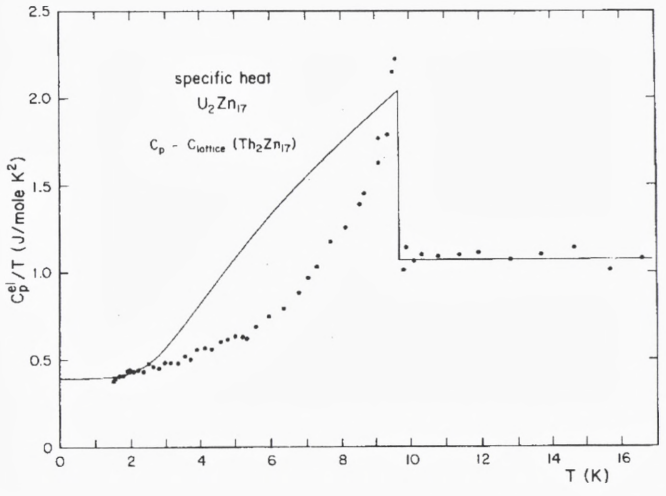


Figure 7. $C_p^{el}/T$ versus $T$ for $U_2Zn_{17}$ between 1.5 and 16 K. The solid line is a BCS-type curve taking into account a non-zero electronic contribution below $T_N$.

the U ions.

The temperature dependence of the magnetic susceptibility $\chi(T)$ suggests that the transition is to an antiferromagnetically ordered state. Although the high temperature part of $\chi(T)$ cannot really be described by a simple Curie–Weiss type law, the general features, nevertheless, indicate a rather strong antiferromagnetic coupling via a seemingly negative paramagnetic Curie temperature. At low temperatures, $\chi(T)$ reveals a maximum at approximately 17 K and a discontinuous slope change at the temperature where the specific heat varies discontinuously. Very similar features have also been observed for the temperature dependence of the electrical resistivity $\rho(T)$.

Measurements employing microscopic techniques confirm the antiferromagnetic character of the ordered state. Neutron diffraction experiments (Cox et al., 1986) and $\mu$SR measurements (Barth et al., 1986) have been made to probe the phase transition and the ordered state of $U_2Zn_{17}$. The neutron results suggest a rather simple magnetically ordered structure below $T_N$. Because the chemical unit cell contains two U atoms, it is identical with the magnetic unit cell. For the saturated ordered moment in zero magnetic field a value of 0.8 $\mu_B$/U has been deduced and its orientation is claimed to lie in the basal plane of the rhombohedral crystal lattice. The magnitude of the staggered moment is distinctly smaller than expected for either free $U^{3+}$ or $U^{4+}$ ions. Somewhat different conclusions were drawn from the experimental $\mu$SR data. They seem to reveal a magnetically inhomogeneous

state (Schenck et al., 1991) and do not confirm the relatively simple picture that is imposed by the neutron results, although both types of experiments have been made using exactly the same single-crystalline sample.

Rather unusual features emerged from a study employing inelastic neutron scattering (Broholm et al., 1987a). First, no evidence for propagating spin waves could be identified, although a scattering intensity due to magnetic excitations is clearly observed. The observation of only a single ridge of intensity parallel to the $\omega$ axis and the failure to identify two branches commonly associated with propagating spin waves is not a resolution problem. This follows from considering the $T^3$ term in the specific heat and the available instrumental resolution. We also note that the broad magnetic excitation spectra persist to energies considerably exceeding $kT_N$. For the analysis of constant $\mathbf{q}$ and constant $\omega$ scans, a rather simple model for the generalized susceptibility has been used successfully. The susceptibility $\chi_{\mathbf{q}}(\omega)$ was approximated by assuming an effective single-ion susceptibility $\chi_0(\omega)$ and a nearest neighbour RKKY coupling $J'$ . Fitting the neutron data on the basis of this model suggests that the phase transition is driven by the temperature dependence of $J'$ rather than by a strong increase of $\chi_0$ , as is usually the case. Concomitant with the transition a sizeable increase of the fluctuation rate is observed, compatible with the decrease of the specific heat $\gamma$ parameter.

Finally we should like to point out that the antiferromagnetic ordering of $U_2Zn_{17}$ is extremely sensitive to impurities replacing Zn on the anion sites (Ott et al., 1989), much more than what is encountered for conventional antiferromagnets. This may be seen from specific heat data that are shown in Fig. 8 and which were obtained by substituting about 2% of the Zn atoms by Cu. Susceptibility measurements down to 0.02 K indicate that this variation of chemical composition is sufficient to suppress magnetic order above this rather low temperature(Willis et al., 1986). The large electronic specific heat above $T_N$, however, is not much affected by the presence of these impurities. Because of the absence of magnetic order, the $C_p^{\mathrm{el}}/T$ ratio stays large down to very low temperatures, with a distinct trend to further enhancement close to $T = 0$. This observation, together with many others, also stated in the previous section, confirms the general conclusion that properties of heavy electron materials are very often sensitive to even tiny changes in their chemical composition.

## 5 Magnetic order involving small moments

One of the outstanding new phenomena in heavy-electron physics is the occurrence of drastically reduced magnetic moments and the cooperative ordering of such tiny moments at low temperatures. Particularly intriguing is the fact that these small

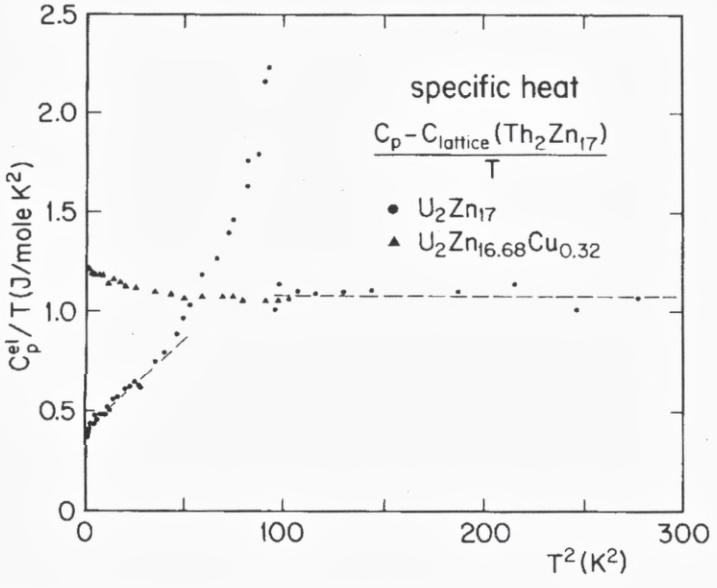


Figure 8. Comparison of $C_p^{el}/T$ versus $T^2$ between pure and Cu-doped $U_2Zn_{17}$ between 1.5 and 16 K.

moments usually derive from ionic moments of expected normal magnitude. The presence of these normal size moments is manifested in the magnitude and temperature dependence of the magnetic susceptibility at elevated temperatures. Even when considering crystal electric field effects, the low-temperature magnetic moments of rare-earth and actinide ions of interest here, are expected to be of the order of 1 $\mu_B$ per ion. It has been found, however, that moments of much smaller magnitude exist as mentioned, for example, in Sect. 2 for $CeAl_3$. Even more surprisingly it has been established that long range magnetic order involving very small moments is possible, first discovered by neutron scattering experiments for $URu_2Si_2$ (Broholm et al., 1987b) and by $\mu$SR measurements for $UPt_3$ (Heffner et al., 1987). In both cases this magnetic order appears to coexist with a superconducting state that sets in at a critical temperature $T_c$ of about one tenth of the antiferromagnetic transition temperature $T_N$. As an example we show the anomalies in the temperature dependence of the specific heat manifesting the transitions of $URu_2Si_2$ in Fig. 9. Neutron diffraction results reveal antiferromagnetic order in this compound below 17 K, among moments with values of a few hundredth of a Bohr magneton (Broholm et al., 1987b). The development of the elastic magnetic scattering intensity with decreasing temperature is shown in Fig. 10. The moments

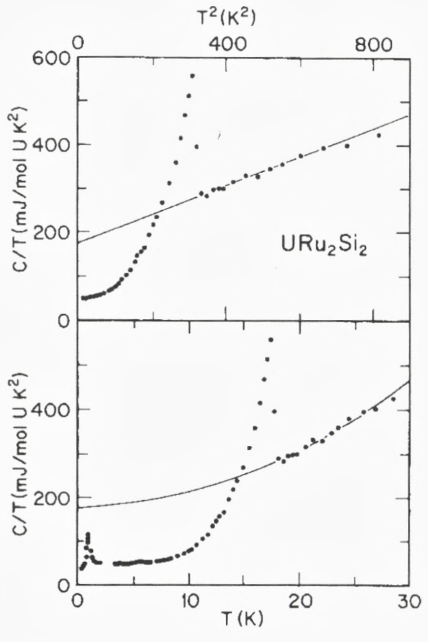


Figure 9. Low-temperature specific heat of $URu_2Si_2$ as $C/T$ versus $T^2$ (upper part) and versus $T$ (lower part) (see Palstra, 1986).

are aligned parallel to the tetragonal $c$ axis of the crystal lattice. While for $UPt_3$ the onset of magnetic order among moments of a few hundredth of a Bohr magneton (Aeppli et al., 1988) finds no manifestation in the temperature dependence of thermal or transport properties, as might be expected, the situation is quite different for $URu_2Si_2$. The transition at 17 K is very well discernible by a large $C_p$ anomaly at $T_N$, as shown in Fig. 9. The entropy loss in this phase transition is obviously not compatible with the measured size of the staggered moments and in spite of many efforts it is still a puzzle how this discrepancy can be explained. From Fig. 9 it may also be seen that via this phase transition, again the $C_p/T$ ratio measured above $T_N$ is sizeably reduced at temperatures well below $T_N$. The resulting electronic subsystem with this reduced effective mass of the quasiparticles has been found to undergo a transition to a superconducting state at approximately 1 K (Schlabitz et al., 1986; Palstra et al., 1985). This superconducting state coexists with the magnetic order, the same situation is met for $UPt_3$.

Theoretically the issue of how these very small moments may develop and be stable seems quite challenging. Some suggestions have been made (Coleman et al.,

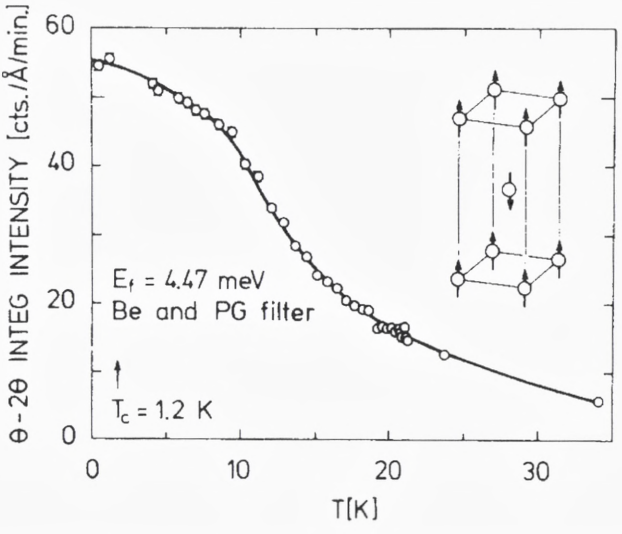


Figure 10. Integral elastic scattering at (100) as a function of temperature for $URu_2Si_2$ (see Broholm et al., 1987b).

1991; Cooper et al., 1992; Barzykin et al., 1993; Santini et al., 1994; Miranda, 1996) but it is not certain that the correct answer has been found yet. At any rate, the increasing number of examples where these very small moments are claimed to have been observed should be motivation enough to pursue this problem further.

In this section we have mentioned the coexistence of antiferromagnetic order involving strongly reduced moments and an electronic subsystem whose excitations are described by quasiparticles with fairly enhanced effective masses. Below we discuss the case of $CePd_2In$, an example where weak interactions of similar magnitude but with opposite influence lead to distinct features in physical properties at low temperatures for which a fairly complete set of data exists.

$CePd_2In$ crystallizes with the hexagonal $GdPt_2Sn$ structure with two formula units per unit cell (Xue et al., 1993). A phase transition at 1.23 K is indicated by anomalies of the specific heat, the magnetic susceptibility and the electrical resistivity (Bianchi et al., 1995) The temperature dependence of the magnetic susceptibility suggests that the transition is to an antiferromagnetically ordered state. At temperatures well below $T_N$, both $C_p(T)$ and $\rho(T)$ reveal the presence of quasiparticles with an enhanced effective mass. In the electronic contribution $\gamma T$ to $C_p(T)$ of $CePd_2In$ above $T_N$ the $\gamma$ parameter is of the order of 30 mJ/mole$K^2$, about five times larger than that of $LaPd_2In$. In spite of the intermediary transi-

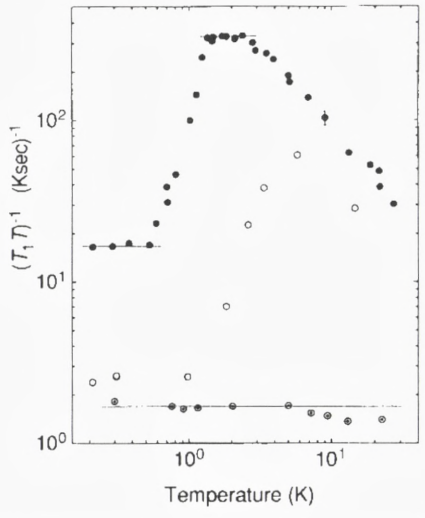


Figure 11. Temperature dependence of the NQR spin–lattice relaxation times of $CePd_2In$ (full circles) and $LaPd_2In$ (dotted circles), plotted as $(T_1T)^{-1}$ versus $T$ on logarithmic scales. Open circles denote NMR data for $CePd_2In$ in a field of 4 T. The dotted lines indicate Korringa type behaviour.

tion to a magnetically ordered state, the $\gamma$ parameter of $CePd_2In$ well below $T_N$ is about 140 mJ/mole$K^2$. This suggests that the electronic correlations in the itinerant charge-carrier system increase substantially with decreasing temperature and persist down to $T = 0$ K although magnetic order sets in at $T_N$ in this temperature range. Thus we meet an obviously quite different situation than that we discussed above for $U_2Zn_{17}$.

More recent NQR and NMR experiments (Gavilano et al., 1995b; Vonlanthen et al., 1996) confirm the antiferromagnetic order and suggest that the ordered moment is only of the order of 0.1 $\mu_B$/Ce. Above $T_N$ the NQR spin–lattice relaxation rate $T_1^{-1}$ is extremely high and obviously due to strong magnetic fluctuations but is reduced by about 95% through the transition (see Fig. 11).

Compared to $T_1^{-1}$ of $LaPd_2In$ below 1 K, the value for the Ce compound is still enhanced by a factor of 10 and the Korringa-type temperature dependence suggests that this is due to the above mentioned electronic correlation effects. It is interesting to note that this enhancement can almost be neutralized by the application of an external magnetic field of the order of 4 T (see Fig. 11). It appears that a magnetic field of this magnitude quenches both the antiferromagnetic order and the interaction that leads to the suppression of the magnetic moments, implying

that these different interactions are indeed of about the same order of magnitude and rather weak. Therefore a clear separation of their individual influences is not possible, an obvious nightmare for any theoretical treatment of this situation.

# 6 Magnetism and superconductivity in heavy-electron materials

The large enhancement of the effective masses of quasiparticles in heavy-electron materials is intimately related with the presence of electronic states with $f$-symmetry. Depending on not well understood circumstances, electrons occupying these states can either contribute to the formation of magnetic moments or may be involved in the formation of Cooper pairs and hence superconductivity. It is therefore not surprising that magnetism and superconductivity of these materials are intimately related, at least phenomenologically.

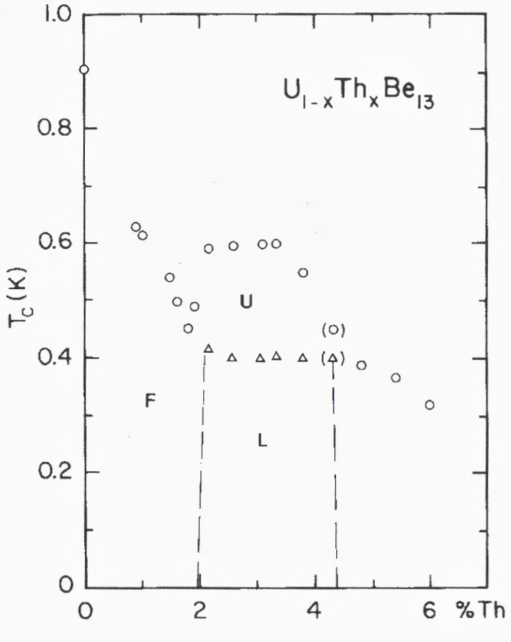


Figure 12. $[x, T]$ phase diagram for superconducting $U_{1-x}Th_xBe_{13}$.

Two examples, $UPt_3$ and $URu_2Si_2$, where magnetic order, although among tiny moments only, and superconductivity appear to coexist have been mentioned in Sect. 5. Coexistence of magnetic order and superconductivity has been claimed to occur also in $CeCu_2Si_2$ in a narrow range of chemical composition, but recent $\mu$SR experiments (Feyerherm et al., 1995) seem to indicate that the two ordering phenomena rather exclude each other, i.e., some sort of phase separation occurs. If we consider non-unitary states of superconductivity, in which time reversal symmetry is broken, as a manifestation of an exotic form of magnetism, we may mention that some experimental observations and their analysis indicate that such states are realized in superconducting $U_{1-x}Th_xB_{13}$ and, again, $UPt_3$ (Sauls, 1994). In Fig. 12, we show the $T_c(x)$ phase diagram of superconducting $U_{1-x}Th_xB_{13}$, mapped out by measurements of the specific heat (Ott et al., 1986). Various experiments indicate that the three identified phases F, U and L exhibit indeed different physical properties implying three distinct superconducting phases (Lambert et al., 1986; Heffner et al., 1990; Zieve et al., 1994).

Based on the assumption of unconventional superconductivity with an odd parity order parameter that allows for point nodes of the gap function, a Ginzburg-Landau type analysis reproduces the boundaries of this phase diagram quite well (Sigrist et al., 1989), and predicts a non-unitary superconducting state in the region of the L phase. Experimental support that such a state is indeed physically realized in phase L has been provided by $\mu$SR experiments (Heffner et al., 1990).

# 7 Summary

We have selected and presented a few cases that should demonstrate the outstanding magnetic properties of heavy-electron materials. Most of the features that are observed experimentally are not really well understood. The question concerning the stability of magnetic moments in these metallic substances is quite tricky and a comprehensive theoretical description of the features of these materials meets with considerable difficulties because the potential magnetic moments cannot be treated as single impurities since they reside, periodically arranged, on regular crystal lattice sites. In addition, the important interactions which determine the low-temperature behaviour of these substances are usually small and all of about the same order of magnitude. Therefore, common perturbation type approximations seem of little value from the outset.

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