We review the experimental results on heavy-fermion uranium based superconductors and magnets.

The discovery of superconductivity at 0.9 K in UBe$_{13}$ [1] spurred a search for new heavy-fermion materials (superconducting or not) among uranium compounds. There was good reason to believe that analogues to cerium compounds with unusual behavior might be found among uranium compounds due to incipient localization of its f-electrons. The two burning questions of physics were and remain (i) what is the nature of the heavy-fermion ground state and (ii) what is the nature of the mechanism leading to superconductivity and of the superconducting state itself in some such heavy-fermion systems? Shortly after the UBe$_{13}$ discovery, UPt$_3$ was found to be a heavy-fermion superconductor (at 0.5 K) with somewhat different properties [2]. We begin by reviewing the superconductivity of these two compounds.

UBe$_{13}$ crystallizes in the cubic NaZn$_{13}$ structure. The uranium atoms occupy a simple cubic lattice with a U–U separation of 5.13 Å, there being no U–U near neighbors. Some of the unusual properties of this interesting compound are shown in fig. 1.

The room-temperature resistivity of 140 μΩcm increases on cooling to a well defined, quite narrow peak of 240 μΩcm at 2.5 K, followed by a drop-off of about 40 μΩcm which is intercepted by $T_c$ at 0.9 K. We also see that the high temperature magnetic susceptibility is Curie–Weiss-like with an effective moment of $\mu_{\text{eff}} = 3.1 \mu_B$, which at low temperature goes into a finite limit as $T$ approaches $T_c$. Note that $5f^2$ and $5f^3$ would give approximately $3.6\mu_B$ in L–S coupling. Below 10 K, where the susceptibility is going towards a limiting value, a plot of $C/T$ vs. $T^2$ (fig. 2) shows that $\gamma$ is rising rapidly from a value above 10 K of roughly 200 mJ/mol U K$^2$ towards 1.1 mJ/mol U K$^2$. The detail of the specific heat anomaly (fig. 3) at $T_c$ indicates both that the superconductivity is a bulk effect, and that it develops in the high density of states band. We note that entropy is closely balanced by a linear extrapolation of $\gamma$ from above $T_c$ to $T = 0$ K, and additionally,
that this low temperature \( \gamma \) happens to accurately account via the expression for Pauli paramagnetism for the entire low temperature limiting magnetic susceptibility. The build up of \( \gamma \) coincides with the loss of local moment behavior.

That electrons in such a highly correlated state could become superconducting is remarkable in view of a (seemingly) higher likelihood of magnetic ordering, and is, of course, very similar to the first observed case of such superconductivity found in CeCu\(_2\)Si\(_2\) [3]. The sample problems plaguing work with CeCu\(_2\)Si\(_2\) are not present in UBe\(_{13}\).

One point to be made here is that the superconductivity in UBe\(_{13}\) differs in a fundamental way from what one observes in the Chevrel phases and ternary rare earth rhodium borides. There one has different sets of electrons, one set trying to superconduct, the other trying to become magnetic. In UBe\(_{13}\), this situation does not seem to occur and it is interesting that none of the rare earth beryllium thirteens becomes superconducting. There is at present no general agreement as to how the heavy-fermion state should be described microscopically and, indeed, it is not clear that the physics underlying CeCu\(_2\)Si\(_2\) and UBe\(_{13}\) will prove to be identical. We note that both the photoemission [4] and the inelastic neutron scattering data [5] differ qualitatively for the two compounds. Again, there is a large sample dependence in the properties of CeCu\(_2\)Si\(_2\) which is absent in UBe\(_{13}\), a very glaring difference between the two systems.

In regards to the question of the nature of the superconductivity we can say the following. It is, first of all, much easier for theorists to accept a new mechanism than a new state, namely odd parity superconductivity. Several suggestions have been put forward for a new mechanism [6]. The problem with a new pairing arises because we have in UBe\(_{13}\) a situation where the electronic mean free path appears to be much shorter than the superconducting coherence length, and this is believed to be extremely harmful to an anisotropic state. This coherence length estimate comes from an analysis of the upper critical field data [7], where the initial slope at \( T_c \) has the record value of \(-420\) kOe/K.

One might be inclined to take seriously this theoretical scruple concerning the short electronic mean path were it not for the surprise contained in experiments on \( U_{1-x}Th_xBe_{13} \) alloys (fig. 4). Not only is \( T_c \) not steadily depressed as \( x \) increases [8], but in the flat region of \( T_c \) vs. \( x \), two bulk specific heat anomalies are observed, the upper one being definitely a superconducting transition. There appears to be a slight excess entropy associated with this transition. NMR experiments [9] through these two transitions show nothing obvious at the low transition, making a magnetic or structural phase change a slim possibility for the second transition. The evidence

![Specific Heat vs. Temperature](image1.png)

**Fig. 3.** Comparison of superconducting specific heat anomaly in UBe\(_{13}\) with strong coupling ABM p-wave calculation [10].

![Specific Heat vs. Temperature](image2.png)

**Fig. 4.** Low temperature specific heat of a \( U_{0.967}Th_{0.033}Be_{13} \) polycrystal, inset schematically shows depression of \( T_c \) with Th addition to UBe\(_{13}\).
as it stands now is consistent with both transitions being superconducting transitions, and this is only easily understood within the context of $l \neq 0$ pairing superconductivity. We further note that the specific heat in the superconducting state of pure UBe$_{13}$ obeys a power law rather than an exponential law, which, coupled with the strong coupling nature of the specific heat jump at $T_c$, is again evidence for zeroes of the gap on the Fermi surface consistent with $l \neq 0$ superconductivity [10]. (As Anderson has emphasized [6], time reversal and parity are the only reliable symmetries where we have strong spin–orbit coupling so that odd-parity is the appropriate term here for superconductivity.) This conclusion contrasts with that of Steglich in regards to CeCu$_2$Si$_2$, where he argues that one has conventional superconductivity [11].

The properties of UPt$_3$ (fig. 5) appear at first sight to be rather different than those of UBe$_{13}$, but it should be borne in mind that the underlying physics is not so clearly of a different sort. UPt$_3$ crystallizes in the hexagonal stacking of Cu$_2$Au known as DO$_{19}$, the same structure in which we find the heavy fermion (but not superconducting) compound CeAl$_2$. For UPt$_3$, the U–U separation is 4.1 Å with again no near U–U neighbors. A Curie–Weiss law with $\mu_{\text{eff}} = 2.6 \mu_B$ is found at high temperature in the magnetic susceptibility [12], and once again this susceptibility approaches a finite value as $T \to T_c = 0.5$ K. There is, in fact, a large anisotropy in $\chi_c$, the basal plane susceptibility being nearly a factor of 2 larger than the $c$-axis susceptibility at low temperature. There is also a peak in the basal plane susceptibility near 14 K, which has been interrupted as a Pd-type maximum, there being no evidence in specific heat for a phase transition at this temperature [12]. A small hysteresis has been seen in ultrasound experiments by Batlogg and Bishop in this temperature region [13] so for the present we should be cautious concerning the interpretation of this peak. It is also interesting to note that Fransen et al. [12] have seen metamagnetic behavior in the basal plane above 15 T at low temperatures.

It happens, curiously, that the vast bulk of the experimental work on this compound has been done on high quality single crystals, either Czochralski or flux grown. Resistance ratios above 200 have been obtained with resistivity at $T_c$ below 1 $\mu$Ω cm, and the resistivity temperature dependence resembles much more that of Al5 compounds than that of UBe$_{13}$ or CeCu$_2$Si$_2$.

The first point to notice about the low temperature specific heat is the turn up (below 7 K) in $C/T$ vs. $T^2$, approaching $\gamma = 450$ mJ/mol U K$^2$ at $T = 0.5$ K, somewhat more than a factor of 2 below that of UBe$_{13}$. In contrast to UBe$_{13}$, the data here can be fitted with a $T^3 \ln T$ term [2] generally associated with ferromagnetic spin fluctuations. That such fluctuations can co-exist with superconductivity sparked much of the interest in UPt$_3$. It is worth pointing out, however, that it is surprising that the fit is valid over such an extended temperature range, and in this connection we also note that the limiting magnetic susceptibility in the $c$-direction agrees with the Pauli value expected from the low temperature $\gamma$, while in the basal plane it is a factor of 2 larger than this. No region of $T^2$ variation of resistivity is found to 20 mK.

The specific heat anomaly at $T_c$ is only about 30% of BCS. This is, however, reproduced in samples from different sources, and the high quality of the samples (single crystals with high resistance ratios) suggests that this small anomaly may well be an intrinsic property of the pure substance. Recent Meissner effect measurements [14] show, in particular, that the superconductivity is a bulk effect.

The most interesting properties measured in the superconducting state are the anisotropy of the upper critical field [15] and the ultrasound absorption in the normal and superconducting states [16]. In this last measurement, a very good $T^2$ (rather than an exponential) behavior is found suggesting zeroes of the gap on
the Fermi surface. Varma has analyzed the experiments as evidence for polar p-wave superconductivity.

There are various ways to get such a power, rather than exponential, law below \( T \) with s-wave superconductivity [17], and it seems likely that no single experiment will prove that one or both of the above superconductors is not s-wave.

The occurrence of superconductivity in such materials naturally raises the question of what other ground states might be possible for heavy-fermion systems. Both spin density and charge density waves would seem likely candidates. We discuss below two systems which appear to order magnetically.

Data on \( U_2Zn_{17} \) are shown in fig. 6 [18]. In this rhombohedral material (U−U separation 4.39 Å) the electrical resistivity is large and increases on cooling below room temperature, reaching a broad maximum near 16 K, below which it falls by a factor of 80, this drop being accentuated below 9.8 K, the antiferromagnetic magnetic ordering temperature identified by specific heat and magnetic susceptibility measurements.

Subtraction of the lattice specific heat of \( Th_2Zn_{17} \) from the \( U_2Zn_{17} \) data gives a nearly temperature independent \( \gamma \) above 9.8 K of 504 mJ/mol U K². The magnetic transition is almost BCS-like in appearance with no apparent short range order above \( T_N \), and \( \gamma \) falls to a limiting value of 198 mJ/mol U K², indicating involvement of a large part of the Fermi surface in the transition. The net entropy through the transition is 1.37 J/mol U K, to be compared with \( R \ln 2 = 5.76 \) J/mol U K. It is possible that a strong coupling version of the Fedders–Martin theory [19] with strongly renormalized interaction might describe this transition. We note there are some similarities with results in NpSn₃ [20]. It is also interesting that the specific heat at the lowest temperatures in the ordered state is proportional to \( T^3 \).

Some similar features are shared by the cubic compound \( UCd_{11} \) (fig. 7) [21], where the U−U separation is 6.56 Å. Again one has a large slowly varying resistivity at high temperature. In this case there is a shallow minimum near 150 K. Below a broad maximum near 80 K, there is an increasingly steep fall off in resistivity with a distinct break near 5 K. The specific heat gives clear evidence for a phase transition here, and the magnetic susceptibility behavior in this region is consistent with some kind of antiferromagnetism. Above 100 K, a Curie–Weiss type behavior is found with \( \mu_{eff} = 3.45 \mu_B \).

From the region above \( T_N \), we extract a specific heat \( \gamma = 840 \) mJ/mol U K². There seems to be considerable short range order in this case. Below the phase transition, \( \gamma \) is reduced to above 250 mJ/mol U K², so again we have a large part of the Fermi surface involved. The shape of the \( C/T \) vs. \( T^{-3/2} \) plot below \( T_N \) is peculiar, and we have no immediate explanation for this. And as in the case of \( U_2Zn_{17} \), we find an excess entropy for the transition, in this case equal to 0.28 \( R \ln 2 \).

So it is clear that magnetically ordered ground states are also possible in these heavy electron systems. It is possible that the interactions involved in the superconductivity are of the same kind that lead to magnetism, and only the ratio of the strength of these interactions decides the ground state. The resolution of this awaits further work. It is curious, in this regard, that all U-based heavy-fermion systems so far discovered with \( \gamma \)
above that of UAl$_2$ ($= 150$ mJ/mol U K$^2$) [22] show some kind of order at low temperature. This is not so for Ce-based compounds, where order seems to be the exception. Admittedly, the sample set is not large.

The clear problem at present is to find a theoretical description of the heavy-fermion state. To date, very few experiments have probed the microscopic aspects, and we know next to nothing about the dynamics.

This work was performed under the auspices of the U.S.D.O.E.

References

W.J.L. Buyers, H.A. Mook and S.M. Shapiro, private communication.