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HEAVY FERMION BEHAVIOR IN URANIUM COMPOUNDS

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The low-temperature behavior of the known heavy-fermion uranium compounds is discussed, and the current situation with respect to unusual superconducting and magnetic states in these compounds is reviewed.

1. Introduction

It was the idea of Hill [1] that a meaningful distinction could be made between uranium intermetallics with U–U separations greater than and less than 3.4 Å. For the latter, 5f electron overlap between neighboring U atoms would lead to f-band formation and loss of 5f magnetic moment; U–U separations larger than 3.4 Å gave 5f local moments and consequent magnetic ordering at low enough temperatures. This thinking led to the Hill plot in which ordering temperature (magnetic or superconducting) is plotted versus U–U separation, and it seemed to be true that superconductors and magnets were separated by this Hill limit of 3.4 Å.

In a number of cases U compounds in the magnetic region were found to be non-magnetic. Detailed experimental and theoretical studies on a number of such Cu_3Au U-compounds [2,3] determined that 5f electrons of U in these were strongly hybridized with neighboring non-f ligands.

The occurrence of heavy fermion behavior in the compounds $CeAl_3$ [4] and $CeCu_2Si_2$ [5], which is certainly closely tied to the Ce 4f electrons, raised the question whether 5f's might not also exhibit similar behavior. After finding UBe_{13} the obvious place to look was in U compounds beyond the Hill limit which did not appear to order magnetically at low temperatures,

but showed some kind of Curie–Weiss magnetic behavior at high temperature. We review part of this effort in this paper.

2. General properties

The earmark of heavy fermion behavior is an enormous low temperature electronic specific heat coefficient γ. There is general agreement that these anomalously large γ values are due to f electrons, so that it makes sense to normalize per f atom. We arbitrarily choose here to classify as heavy a U compound whose γ exceeds 100 mJ/mol-UK^2. The U compounds for which data have been published meeting this criterion are listed in table 1.

If this large γ really is giving a measure of the electronic density of states at the Fermi level in these intermetallics, then the corresponding band width of the heavy electrons must be extremely narrow, some tens to hundreds kelvin. This narrow band width is consistent with what is seen in the magnetic susceptibility and other aspects of the low temperature specific heat. It is important to keep in mind that many body effects will make important contributions to these properties. In the magnetic susceptibility one finds at high temperature a quasi Curie–Weiss law with negative intercepts which

Table 1

Compound	γ (mJ/mol-UK^2)	γ_V (mJ/cm^3)	Ordering
USn$_3$ [a]	169	2.84	n(spin-fluct.)
UAl$_2$	150	4.25	n(spin-fluct.)
UCu$_5$ (UAgCu$_4$)	> 250 (310)	> 4.80 (5.95)	T_N = 15 K (18.15 K)
U$_2$Zn$_{17}$	500	5.08	T_N = 9.6 K
UCd$_{11}$	840	5.21	T_N = 5 K
UPt$_3$	450	10.59	T_S = 0.54 K
UBe$_{13}$	1180	13.55	T_S = 0.9 K

[a] M.B. Brodsky, Rep. Prog. Phys. 41 (1978) 103.
Published data for U compounds whose γ exceeds 100 mJ/mol-UK^2

goes over at low temperature to a large constant value. In a C/T versus T^2 plot of the specific heat (fig. 1) it is clear that the large γ is only developing at low temperatures. Both of these measurements are suggestive of a change from a non-degenerate to a degenerate electron gas as T decreases. It is also instructive to plot the limiting low temperature γ's versus the corresponding χ's (fig. 2). The line drawn in the plot represents the free electron correspondence between γ and χ. It is worth noting that this line seems to give a limiting envelope for the data.

The temperature dependence of the electrical resistivity falls into two types (fig. 3). One is characterized by a Kondo-looking negative $d\rho/dT$ above a large low temperature peak, below which the resistance falls sharply. This low temperature drop is often loosely referred to as the onset of coherence. The other type of temperature dependent resistivity is quite similar to the resistivity characteristic of high T_c Al5 superconductors such as Nb$_3$Sn: a rapid rise in resistivity at low T
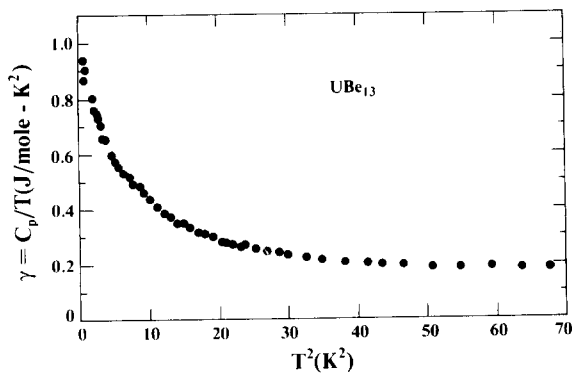
followed by a weak T dependence above $\approx$ 150 K. For both cases the room temperature resistivity is large, of order 100 $\mu\Omega$cm. It is possible that both cases arise from the same physics, and that the peak seen for the first type has merely been pushed to high temperatures in the second type. It is also interesting that there is evidence for spin-fluctuation behavior in UAl$_2$ and UPt$_3$ (from specific heat) and both these compounds have the second kind of resistivities.

There are two burning questions connected with these heavy fermion materials: (1) what is the proper theoretical description of the normal state at low tem-
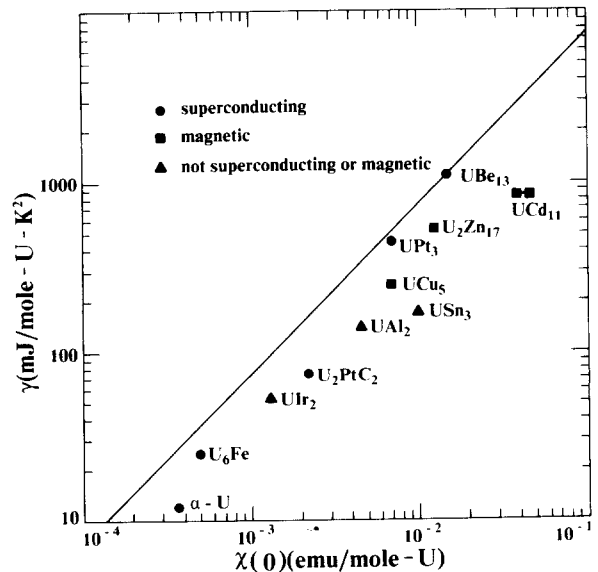

Fig. 1. C/T versus T^2 for UBe$_{13}$.

Fig. 2. Ln γ versus ln χ for uranium compounds.
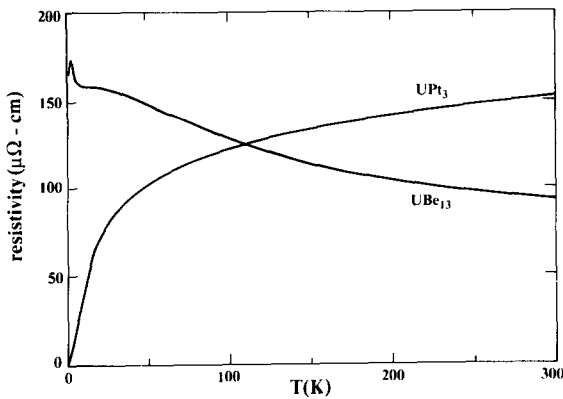
Fig. 3. Temperature dependence of the electrical resistivity of UPt_3 and UBe_{13}.

peratures and (2) are we seeing fundamentally new kinds of superconductivity and magnetism driven by new mechanisms at these extremes in parameter space?

It is hoped that some kind of Fermi liquid description will apply to the heavy fermion state at low enough temperature. This regime is probably reached in the case of the spin-fluctuators UAl_2 [6] and UPt_3 [7] near 1 K where the temperature variation of the electrical resistivity is approaching T^2 as expected for a Fermi liquid (fig. 4) [8]. A point we will come back to again is that spin–orbit effects are expected to be large for U intermetallics and the Fermi-liquid theory would have to include this.

It is not so obvious that U_2Zn_{17}, UCd_{11} and UBe_{13} can be well described by Fermi liquid theory. Ott et al. [9] have used the Brinkman–Rice approach to an almost

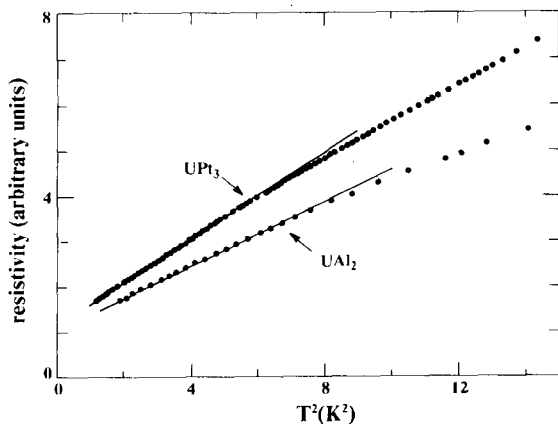Fig. 4. Low temperature T^2 behavior of UAl_2 and UPt_3.

localized Fermi liquid to describe the normal state of UBe_{13}. Other approaches using Anderson lattice [10] and Kondo lattice [11] models have been applied to the heavy fermion problem. Most workers in the field probably agree that some of the physics of Kondo impurities applies, but it is still too soon to comment critically on just how it does. We note here in this regard that an unpublished analysis of the large negative magnetoresistance of UBe_{13} in the normal state at low temperatures by Batlogg finds a good fit to a Kondo type impurity model with a temperature dependent T_K.

3. Superconductivity of UPt_3 and UBe_{13}

We have mentioned that the great excitement over discovery of superconductivity in UPt_3 and UBe_{13} stems from the possibility that either or both the mechanism and pairing may be new because the normal state properties of these compounds make conventional s-wave pairing seem unlikely.

Consider first UPt_3. This material can be prepared as high quality single crystals by several techniques. The low temperature resistivity at $T_c = 0.54$ K is low, less than 1 $\mu\Omega$cm, suggesting an electronic mean free path of several hundred ångström. The specific heat anomaly at T_c is only about 30% of BCS [12]. Measurements on materials prepared by various techniques suggest that this may be an intrinsic property and not the result of poor sample quality. We note that impurities have a drastic effect on T_c [12].

The idea that p-wave (or odd-parity, as pointed out by Anderson [13]) superconductivity might be present in UPt_3 was based on the experimental observation of a T^3 ln T signature of spin-fluctuations in the specific heat [12] (fig. 5). Since spin-fluctuations are thought to be extremely hostile to conventional, but not p-wave pairing, UPt_3 appeared as a good candidate for a new superconducting state. Further evidence for this came from ultrasound attenuation measurements through T_c [14]. A T^2 power law was found below T_c and interpreted by Varma as evidence for a polar p-wave state. A recent calculation by Rodriguez [15] claims this power law is consistent with the ABM state. The topological difference between these two anisotropic superconducting states is that the former has lines on the Fermi surface where the superconducting gap vanishes, the latter points. Group theory argues that the polar state is very unlikely for UPt_3 [16]. This controversy of theory is not yet resolved. It can also still be argued, as with the specific heat anomaly at T_c, that the gapless nature of the superconductivity is a dirt effect. We note in
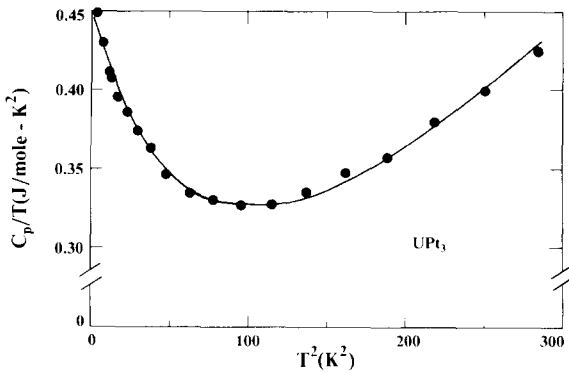
Fig. 5. C/T versus T^2 for UPt$_3$ showing fit with T^3 ln T term.

passing the large initial slope of $H_{c2}(T)$ (-17 T/K) [17] and the relatively large dependence of T_c and H_{c2} on pressure [18].

The situation for UBe$_{13}$ has some additional features. First, the upper critical field has a nearly vertical slope at $T_c = 0.9$ K (fig. 6) [19]. The high value of the electrical resistivity at T_c (≈ 100 $\mu\Omega$cm) makes p-wave pairing seem an unlikely possibility in view of the fact
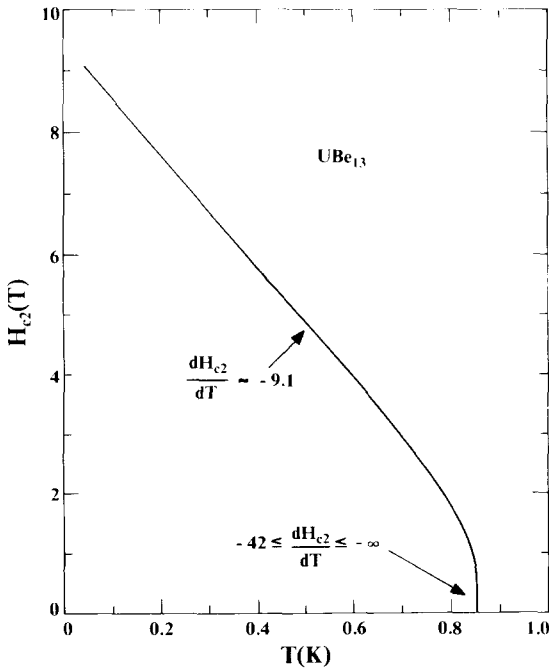

Fig. 6. Critical magnetic field of UBe$_{13}$.

that the scattering implied by this large resistivity would destroy the angular momentum of the pairs. However, it is possible that UBe$_{13}$ is not so dirty as it seems: Cu substitutions on the Be lattice at the level of UBe$_{12.97}$ Cu$_{0.03}$ [20] is sufficient to destroy superconductivity without affecting γ. The large negative magnetoresistivity and the decrease of residual resistivity on alloying with Th also support this conclusion. An additional interesting feature of H_{c2} is that is does not appear to be approaching $T = 0$ with zero slope. An analysis along conventional lines, incidentally, finds a coherence length of ≈ 50 Å [19].

The superconductivity seen in UBe$_{13}$ is definitely in the strong coupling regime as evidenced by the specific heat jump at T_c. In addition, the specific heat follows approximately a T^3 law well below T_c [9], arguing again here for zeroes of the gap on the Fermi surface. This kind of data by itself is equivocal, however, in that power laws have also been seen in strong coupling transition metal superconductors, although the conditions in UBe$_{13}$: pure UBe$_{13}$ are somewhat cleaner in that the lattice contribution to the specific heat is completely negligible compared with the electronic term. It is important to emphasize that the size of the specific heat anomaly at T_c demonstrates that the gap opens in the high density of states band.

The new feature in UBe$_{13}$ comes upon alloying with Th. Between roughly 2 and 5% Th substitution for U, two bulk specific heat anomalies are observed at low temperatures (fig. 7) [21]. Recent specific heat measurements in a magnetic field have shown that in fact entropy is balanced through both these transitions [22]. The immediate question is whether this second transition is superconducting or magnetic.

It is known that these alloys remain superconducting below both transitions. No anomaly has been seen in either H_{c2} [23] or Be NMR relaxation rates [24], making the magnetic possibility somewhat unlikely. However, ultrasonic attenuation is quite different in the alloy compared to pure UBe$_{13}$ has a peak in attenuation just below T_c [25], unlike anything seen in other superconductors, while the Th doped material has an anomaly at the lower transition which is two orders of magnitude larger than the peak near T_c in the pure case [26]. This has been given as evidence that the lower transition is magnetic, in conjunction with a set of critical exponents deduced from the shape of the attenuation spike. For the pure UBe$_{13}$, the attenuation data again point to an anisotropic superconducting state [26], which is also supported by power law data from NMR [24].

The problem presented by the double transitions in Th doped UBe$_{13}$ is unresolved. Neutron diffraction [27]
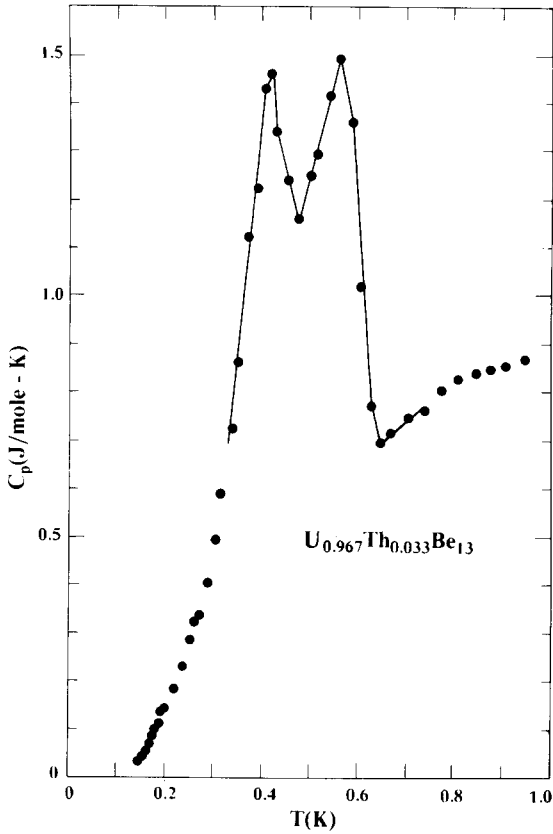
Fig. 7. Low temperature specific heat of $U_{0.967}Th_{0.033}Be_{13}$.

Fig. 8. C/T versus T^2 for U_2Zn_{17} with a lattice term substracted.

has so far found no evidence for magnetic order below the lower transition. It is possible that the second transition involves a different part of the Fermi surface since both the upper and lower transitions give the appearance of being second order.

4. Magnetic ordering in U_2Zn_{17}, UCd_{11} and UCu_5

At low temperature one might expect the heavy fermion state to be unstable relative to several possible orderings: superconductivity, spin density wave or charge density wave. So far there is no reported evidence for a heavy fermion compound showing charge density wave ordering. However, several cases which have been interpreted as spin density waves are known.

U_2Zn_{17} orders at $T_N = 9.6$ K [28] (fig. 8). Above this temperature γ appears to be approximately constant with a value of 500 mJ/mol-UK^2. Below T_N the γ falls
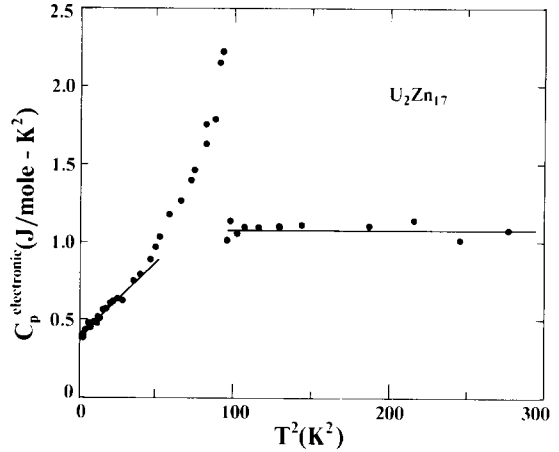
to 190 mJ/mol-UK^2, the low T specific heat varying as $T + T^3$. It appears that approximately 2/3 of the Fermi surface is involved in this condensation. There is a small net negative entropy involved in the transition relative to the extrapolated normal state specific heat.

The properties of UCd_{11} are rather similar (fig. 9) [29]. Here $T_N = 5$ K. The γ is larger, 840 mJ/mol-UK^2. There is a small net excess entropy through the transition, and again approximately 2/3 of the Fermi surface appears to be involved.

While the presence of Cd in UCd_{11} makes neutron work on this compound difficult, this is not true for U_2Zn_{17}. An attempt has been made to find magnetic ordering on a single crystal [30] without success so far.

A further possible example of a heavy fermion magnetically ordered system is UCu_5, with $T_N = 15$ K [31]. This temperature is sufficiently high to make it difficult to determine what the γ really is for the material, although it is probably in excess of 250 mJ/mol-UK^2. As $T \rightarrow 0$, $\gamma \rightarrow 86$ mJ/mol-UK^2. For this compound a commensurate structure of ferromagnetic (III) sheets coupled antiferromagnetically has been found [32]. Similar measurements have been performed by us on $UAgCu_4$, for which the γ below T_N extrapolates to approximately 300 mJ/mol-UK^2.

There is no reported evidence at present to indicate whether or not there is anything unusual about the condensation in these materials. Again, the presence of strong spin–orbit coupling makes it likely that details of the ordered state may be more complicated than in itinerant, transition-metal magnets.

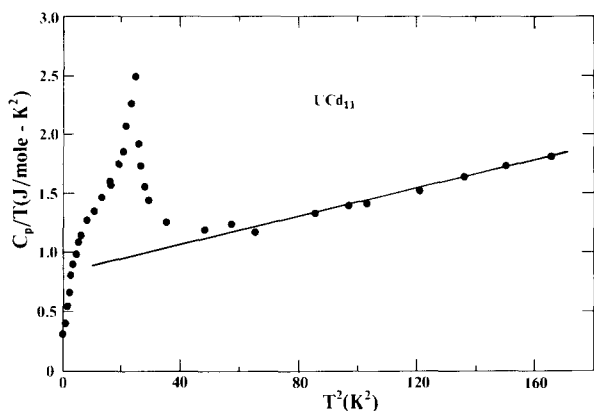One's curiosity is aroused by the seeming haphazard

Fig. 9. C/T versus T^2 for UCd_{11}.

variation of superconductivity and magnetism with γ. Many properties of metals vary smoothly with electron density, and this suggests looking at γ normalized per unit volume, γ_V. The table 1 lists values for the various heavy fermion compounds known. One sees there a rather regular progression from spin-fluctuation systems showing no magnetic order through "magnetically" ordering systems to the superconductors as γ_V increases. The data base for this suggestive progression is small, but the correlation is intriguing.

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