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SUPERCONDUCTIVITY OF HEAVY-ELECTRON URANIUM COMPOUNDS

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The current understanding of the superconductivity of heavy-electron uranium compounds is reviewed. Both the pairing and the mechanism appear to have been established as unusual in UPt_3 and UBe_{13}. Small-moment magnetic ordering is now known to coexist with superconductivity in URu_2Si_2 and UPt_3. The understanding of the properties of UBe_{13} may be viewed as the central problem in heavy-electron physics.

1. INTRODUCTION

The recent developments in the field of superconductivity are focussing renewed attention on novel mechanisms and anisotropic pairings, a situation similar to that which attended the developments in heavy-electron materials. There appear to be a number of similarities between the physics of the cuprates and that of the heavy-electron superconductors, as well as significant differences. Both are highly correlated electronic systems with strong magnetic interactions. There is no evidence as yet to suggest that the mechanism for superconductivity is similar. But heavy-electron superconductivity has served as a very fertile ground for investigating non-phonon mechanisms and higher angular momentum pairings, and this experience has much to tell us. We review here the status of the understanding of superconductivity in uranium heavy-electron compounds.

2. THE HEAVY-ELECTRON NORMAL STATE

A useful qualitative viewpoint for thinking about heavy-electron systems is provided by the Kondo effect. All known heavy-electron materials possess f-electrons which are behaving magnetically like local moments at high (room) temperature. The conduction electrons in these materials compensate the local moments as $T \rightarrow 0$ K, the high temperature entropy of the spin system smoothly transferring to the conduction electron system. In this extreme view, the local f-moments make the conduction electron heavy. If the temperature scale over which this happens is T_K, we estimate the low temperature electronic specific heat $\gamma \sim (k \ln D)/T_K$ per f-moment, where D is the degeneracy of the f-moment.

Bloch's Theorem will apply to the low temperature electronic state of the atomically ordered lattice of f-atoms, a state which should be describable as some kind of correlated Fermi liquid. The large electrical resistivity due to the single ion-type Kondo scattering is observed to be lost below a temperature generally referred to as the coherence temperature, T^*. A rapid change in the Hall constant with temperature also accompanies the development of coherence. It is an unsolved problem of theory to describe the development of coherence.

RKKY-type magnetic interactions between f-moments can both modify T_K and lead to competing magnetically ordered ground states. One way to think about the effect of magnetic order on a heavy electron state is in terms of the internal field produced. The local magnetic field at an f-site due to the long range magnetic order will partially quench the Kondo compensation there. In this view, the loss of γ below a magnetic transition is due to loss of mass.

3. URANIUM COMPOUNDS

The pioneering work of Steglich establishing the bulk nature of the superconductivity of $CeCu_2Si_2$ focussed attention on f-electron materials with large γ's, corresponding to effective masses some two orders of magnitude larger than the electron mass. A strong parallel between the properties of Ce and U intermetallics has been found to exist. There are, however, enough differences of detail between the physics of Ce and U materials to make it desirable to treat only U-compounds here.

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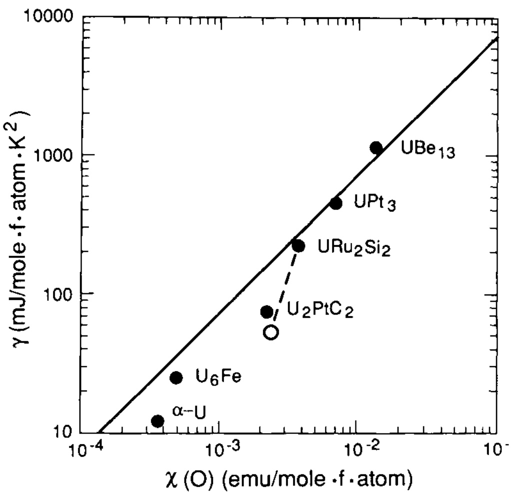

FIGURE 1.
Ln γ versus ℓn χ (for T → 0 K) plotted for Uranium superconductors. The line is the free electron Sommerfeld relation between γ and χ.

There are only a small number of superconductors containing U (Table). A convenient way to present these materials is in a χ-γ plot, Fig. 1. We see that these superconductors are found over the entire range of γ-values known for U-compounds. We point out that the two heavy-electron superconductors UPt_3 and UBe_{13} very nearly obey the Sommerfeld relation between χ and γ.

We discuss the low-γ set of materials first. Elemental U is believed not to be a superconductor at ambient pressure (1). The pressure induced superconductivity of α-U peaks near 2 K at 10 kbar. Neutron scattering experiments have found that a charge density wave develops below about 40 K in α-U, and it is plausible that the pressure effect on T_c is due to suppression of the charge density wave with pressure. The stabilized γ allotrope of U has also been reported to be superconducting (2).

The interesting set of compounds U_6X (X = Mn, Fe, Co and Ni) have γ's in the neighborhood of 25 mJ/mole U-K^2 (3). T_c is highest for U_6Fe, 3.9 K. The close U-U spacings in these tetragonal materials make it likely that strongly hybridized f-bands exist at the Fermi level. This separates the physics of these materials from direct overlap with that of the much larger-γ materials, although it is clear that important correlation effects are present here. No one appears to have been able to prepare single crystals of these easily oxidized, peritectically forming materials.

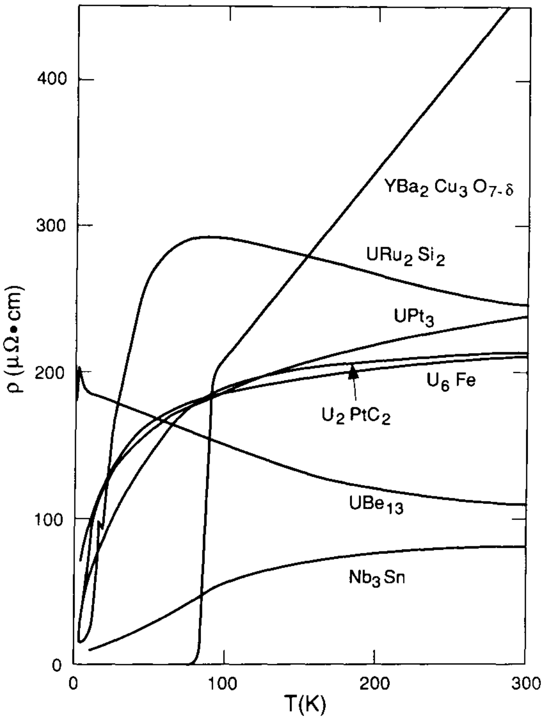

FIGURE 2
Temperature dependence of the electrical resistivity of various superconductors. YBa_2CuO_7 data from (22), Nb_3Sn from (23), U_6Fe from (24), and URu_2Si_2 (25). Other data from references in text.

The tetragonal U_2PtC_2 has a γ = 75 mJ/mole U-K^2 and T_c = 1.5 K (4). The anomalous, bulging shape of the electrical resistivity (Fig. 2), coupled with the substantial γ, place this material in the transitional region between light- and heavy-electron behavior. There has been little work on this material, and no single crystal data exist.

Considerably more attention has been given to URu_2Si_2. This material crystallizes in the tetragonal structure found for $CeCu_2Si_2$, and large single crystals have been produced by several groups. Both the normal state resistivity, most markedly in the basal plane, and the Hall constant decrease strongly in the vicinity of 50 K, suggesting that $T^* \approx 50$ K (5). The Cr-like resistance anomaly at T_N = 17 K has been found by neutron diffraction to correspond to 0.02 μ_B/U simple antiferromagnetic order, the moments aligning parallel to the c-axis (6). At T_N, γ is extrapolated to be 180 mJ/mole U-K^2. This is approximately the value that is found for a large number of U-intermetallics which undergo no low temperature phase transitions. The remarkable feature of URu_2Si_2 is the subsequent development of superconductivity below 1.2 K. At this temperature γ = 75 mJ/mole U-K^2. At the superconducting transition, $\Delta C/\gamma T_c = 1.3$, somewhat reduced from the BCS weak coupling value.

There is still a lot to be understood about URu_2Si_2. Many of the single crystal experiments performed on UBe_{13} and UPt_3 have not been carried out, and these could go a long way towards helping such an understanding. For example, from thermodynamic data it appears that the commensurate magnetic transition at 17 K opens a gap across ~70% of the Fermi surface, a surprisingly large fraction in view of the anomalously small ordered moment. This makes the transition, incidentally, quite different from the magnetic transitions seen in most heavy-electron U-compounds, where it is more likely that the effective mass changes below T_N, rather than the Fermi surface area. The idea, then, is that the superconductivity occurs on what remains of the Fermi surface. This, again, makes URu_2Si_2 appear very different from the heavier electron U-superconductors. It is likely that the real order parameter here has not been found.

4. UPt_3

UPt_3 crystallizes in the same hexagonal structure as $CeAl_3$, the first identified heavy-electron compound. A wealth of data exists on single crystals of this compound, and there is now some concensus that this is an anisotropic superconductor with a magnetic pairing mechanism.

UPt_3 has a strongly bulged, very anisotropic electrical resistivity, much like that of an A-15 transition metal superconductor (Fig. 2). The Hall constant shows a rapid change in the vicinity of 20 K, indicating that $T^* \approx 20$ K (7). The also anisotropic magnetic susceptibility peaks at 17 K in the basal plane, a feature which appears to be related [from neutron experiments (8)] to the development of strong antiferromagnetic correlations, and presumably, coherence. de Haas-van Alphen work has also been reported, finding masses as high as 120 m_e (9). This is a lower limit, set by experimental constraints, on the largest mass on the Fermi surface.

The low-temperature specific heat shows what was believed to be evidence for spin fluctuations but is now interpreted in a more general Fermi liquid context. γ = 450 mJ/mole U-K^2, and the anomaly at T_c is $\Delta C/\gamma T_c \approx 0.8$. This gave rise to the now dead suggestion that the superconductivity was not bulk.

An earmark of anisotropic superconductivity is the presence of power laws in T below T_c in various properties as T→0 K arising from nodes of the superconducting gap on the Fermi surface. In UPt_3, a T^2 dependence was found in both the specific heat (10) and c-axis ultrasonic attenuation below T_c (11). Additional evidence for an anisotropic superconducting state comes from anisotropy of sound propagation in the basal plane, depending on polarization of the sound (12), and tunneling experiments which find no gap in the basal plane (13), but a gap perpendicular to the plane. All these contribute to the idea that UPt_3 is a polar superconductor with a line of nodes of the gap perpendicular to the hexagonal c-axis.

Recent evidence supporting a magnetic pairing mechanism has come from neutron measurements. These experiments have, firstly, found a small moment ordering of 0.02 μ_B/U at 5 K in pure UPt_3 (14). This is the same temperature at which Th and Pd doping induce a much larger magnetic moment (~0.7 μ_B) ordering in UPt_3 (15) and at which $d\rho/dT$ has a maximum. The spin arrangement is the same in the two cases. What is especially interesting is that the unusual mean field like development of the order parameter ($M^2 \propto T_N - T$) below T_N abruptly ceases at T_c = 0.5 K, clear evidence for an interference between the magnetic and superconducting order parameters (Fig. 3). In addition, the energy characterizing the magnetic correlations in this system corresponds to 4 kT_c.

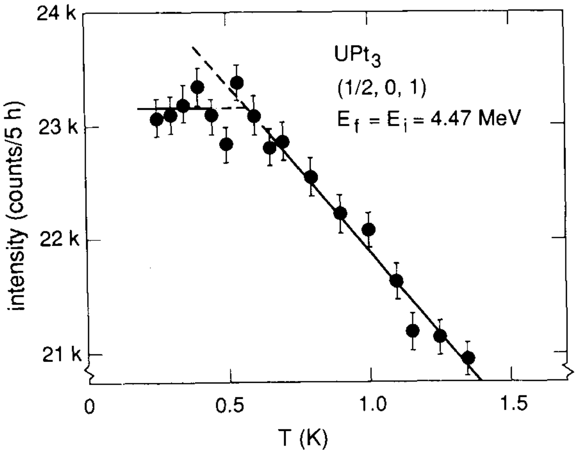

FIGURE 3
Interference between superconductivity and magnetism seen in the intensity of the (1/2, 0, 1) scattering intensity in UPt_3 (14).

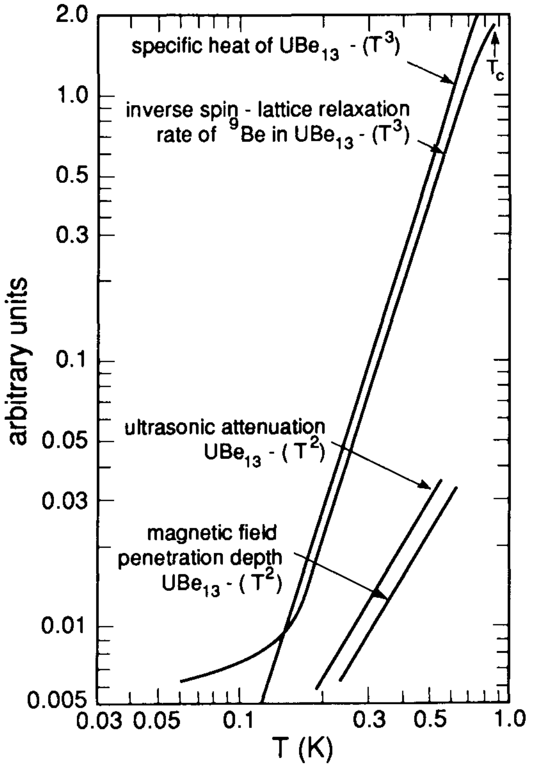

FIGURE 4
Power laws in various properties of UBe_{13} below T_c (26).

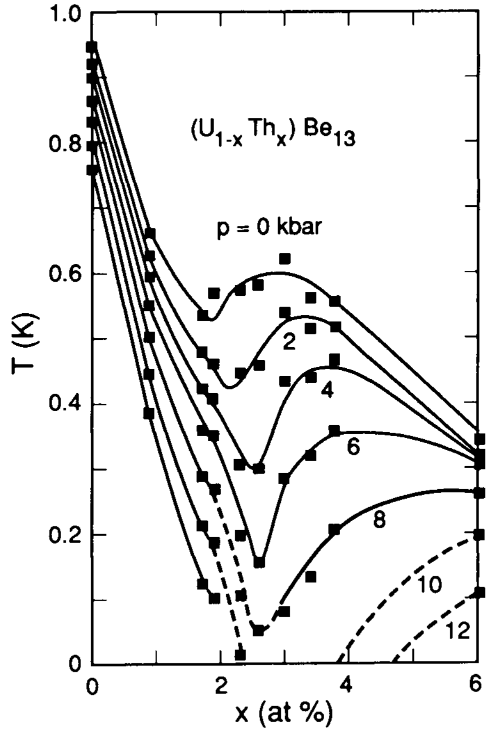

FIGURE 5
Pressure and composition dependence of T_c for $U_{1-x}Th_xBe_{13}$ samples (27).

5. UBe_{13}

UBe_{13} is in many ways a more complex system than UPt_3. The resistance, similar to that of $CeCu_2Si_2$, is Kondo-like, with a sharp peak near 2.5 K. The drop in resistance below this temperature, coupled with a sharp decrease in the Hall constant below 1 K indicate that T^* $\approx$ 1 K, very close to the observed T_c = 0.9 K. The resistance at T_c is still approximately 100 $\mu\Omega$-cm.

The specific heat anomaly at T_c is 50% larger than weak coupling BCS. As T → 0 K, the temperature dependence of the specific heat is consistent with an axial superconducting state having nodes at points on the Fermi surface. This assignment is further supported by temperature dependent London penetration depth experiments which are consistent with the axial state and not with a conventional BCS superconductor (16). Figure 4 shows the power law dependence in various properties below T_c.

Indirect evidence for an anisotropic superconducting state comes from the bizarre behavior of T_c with Th addition. Figure 5 shows the variation of T_c with x in $U_{1-x}Th_xBe_{13}$ and with pressure. The negative cusp in T_c at x = 1.7 a/o Th coincides with the development, at larger x, of a second phase transition as indicated by the specific heat below T_{c1} $\approx$ 0.6 K, at T_{c2} $\approx$ 0.4 K. The very large feature observed in ultrasonic attenuation at T_{c2} (17) suggested that it was associated with an antiferromagnetic transition. Another suggestion is that it is a transition to another superconducting state. Muon experiments suggest a very small moment (~ 0.001 μ_B/U) below T_{c2} (18), but neutron and NMR (19) experiments have not confirmed this. We mention here that superconducting states which carry a moment are possible. Current thinking is that the superconducting state is different on the two sides of the cusp.

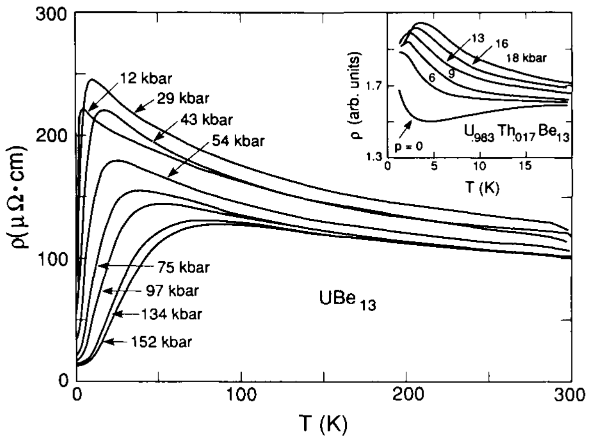

FIGURE 6
Pressure dependence of the temperature dependent electrical resistivity of UBe_{13}. Inset shows data for $U_{.983}Th_{.017}Be_{13}$ at low temperature, in which T_m reappears.

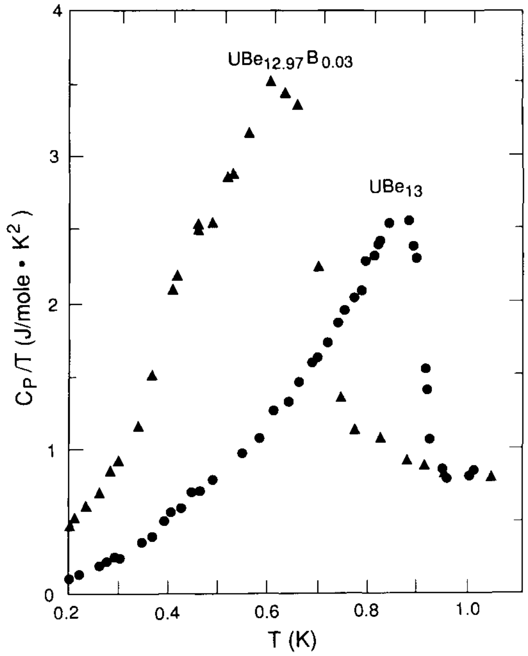

FIGURE 7
Comparison of the low temperature specific heat of UBe_{13} with that of $UBe_{12.97}B_{.03}$ polycrystal.

It so happens that the resistance feature at T_M = 2.5 K correlates with the cusp, in that as x increases, T_M decreases and appears to go through T_c for x slightly less than the cusp concentration. Resistance measurements under pressure show (Fig. 6) that T_M moves to higher T with pressure. So we have a correlation: higher T_M goes with lower T_c, and T_c increases for x > 1.7 a/o Th because T_M is below T_c. However, T_M does not appear to be "responsible" for T_{c2}. $dT_M/dP > 0$, while $dT_{c2}/dP < 0$ (20). A better way to think about the peak is, perhaps, that when it moves to lower T, these other phase transitions can happen. It is interesting to note that there is a rounded maximum in C in the vicinity of the resistivity peak in pure UBe_{13}.

Th is the only substitution for which this curious behavior is definitely established. There is the possibility that something similar happens with B additions for Be. We can see in Fig. 7 that the specific heat anomaly at T_c is very large with B doping and it is not clear that entropy can be balanced. The question arises, of course, as to why Th has this kind of effect. It does appear that γ is an increasing function of Th content, at least for x at the several percent level. We note further that Gd added to $U_{1-x}Th_xBe_{13}$ depresses T_c at differing rates depending on whether x is > or < 1.7 a/o Th.

The effects of pressure on the normal state of UBe_{13} is to decrease γ much more rapidly than χ, so that its point on the χ-γ plot moves well below the Sommerfeld line with pressure. T_c drops at the same time. One possibility is that magnetic fluctuations increase. The very high pressure resistivity actually has a shape very similar to that of UPt_3 (Fig. 6.).

6. FINAL REMARKS

The large γ's present in UPt_3 and UBe_{13} are of clear magnetic parentage. Neutron measurements at low temperature on both these materials show the presence of antiferromagnetic correlations. The fact that superconductivity can occur in such systems is surprising and suggests an underlying magnetic mechanism for T_c. The data pointing to zeros of the superconducting gap on the Fermi surface are suggestive of a different pairing, which is consistent with, but not required by, a non-phonon mechanism.

The occurrence of superconductivity in high-γ materials seems to be quite rare. Large γ's require small T_K's, either because T_K is naturally small or the RKKY interaction moves it there (21). If T_K is small, magnetic order will dominate in most cases, making superconductivity less likely. The problem presented by the small-moment ordering in the superconductors and other heavy electron compounds can be classed as completely without understanding. The heavy electron materials remain interesting as the archetypal clean systems where there is an obvious competition between superconductivity and magnetism for the same electrons.

We acknowledge experimental assistance of E. Felder and useful discussion with B. R. Coles.

TABLE

Superconductor	γ(mJ/mole U-K^2)	T_c(K)
α-U	9.6	2.4
$U_{.82}Mo_{.18}$		2.11
U_6Mn		2.32
U_6Fe	25	3.9
U_6Co		2.3
U_6Ni		.86
U_2PtC_2	75	1.47
URu_2Si_2	75	1.2
UPt_3	450	.54
UBe_{13}	825	.9

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