Heavy Fermion Superconductivity: 5f vs 4f

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Heavy electron materials are the only class of materials in which we know where to look for superconductivity. We discuss the relation between single ion and dense Kondo heavy electron physics, what sets the energy scale in these materials, the ways in which their low temperature exotic superconductivity is a prototype for all highly correlated electron superconductivity and the similarities between the 4f and 5f heavy Fermion materials.

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Much of the interest in heavy Fermion and other highly correlated electron materials centers around their superconductivity, in particular when and where it occurs. There exists of course the desire to place all highly correlated electron superconductivity within a single framework, and our intent here is to compare 5f and 4f heavy Fermions with this in mind while also keeping in mind the much higher $T_C$’s found among transition metal materials.

What one might call the standard model of heavy Fermion superconductivity begins with the observation that almost all Ce-based heavy Fermion superconductors appear in the vicinity of an antiferromagnetic quantum critical point. A well studied example of this is shown in Fig. 1. While one cannot say with certainty that proximity to a quantum critical point is true for all heavy Fermions with this in mind while also keeping in mind the much higher $T_C$’s found among transition metal materials.

In the vicinity of an antiferromagnetic quantum critical point the specific heat typically varies as $T \ln(\frac{T^*}{T})$ with coefficient of order $\frac{R \ln 2}{T^*}$, which gives an entropy of $R \ln 2$ at $T^*$. We observe that $T^*$ appears to the scale for the superconducting transition temperature $T_C$ in that $T_C/T^*$ is of order 1/20, similar to the ratio of $T_C$ to the Debye $\theta$ one sees in phonon coupled BCS superconductors.

A tenet of the standard model of heavy Fermion superconductivity is that the so-called glue of Cooper pairing comes from the magnetic fluctuations residing in the dense Kondo liquid. This means that both the magnetic order and superconducting order which are seen competing in Fig. 1 utilize the same fluctuation spectrum. The interesting feature we see in Fig. 1 is that when the antiferromagnetic transition temperature $T_N > T_C$, superconducting order and antiferromagnetism can coexist at some lower temperature. However, the reverse is not true: there is no co-existence when $T_C > T_N$. The simple explanation for this is that the superconductor gaps out the low energy part of the magnetic fluctuation spectrum which favors the antiferromagnetic order.

Data [2] on the 2.3 K ambient pressure superconductor CeCoIn$_5$ support this assertion. The entropy developed to $T_C$ is approximately $0.15R \ln 2$ per Ce. At $T_C$,
Fig. 1. (Color online) Temperature - pressure phase diagram of the pressure induced heavy Fermion superconductor CeRhIn$_5$ [1].

\[
\frac{C}{T} \propto \ln T
\]

Typically: \( C/T = (R\ln 2/T^*)\ln(T/T^*) \)

and \( S(T^*) = R\ln 2 \)

\( T^* \) sets the scale for heavy Fermion physics

For heavy Fermion superconductors:

\[ S(T_C) \sim 10-20\% \ R\ln 2 \iff T_C/T^* \sim 1/20 \]

the jump \( \Delta C/\gamma T_C = 5 \), much larger than weak coupling BCS. However, if one integrates \( \int \gamma dT \) out to \( T_C \) and compares this to \( \Delta C \), one gets a value much closer to weak coupling, \( \Delta C/\int \gamma dT = 2 \). We also have the data of Sparn et al. [3] shown in Fig. 3 for the dependence of \( \Delta C/\gamma T_C \) on pressure. This drop in the specific heat jump with pressure corresponds to the pressure variation of an intrinsic residual resistivity which essentially vanishes at the same pressure where \( T_C \) becomes a maximum seen in Fig. 4 [4]. A consistent way to think about this is that one has a residual resistivity arising from the remaining uncondensed Kondo centers and that pressure reduces their concentration to zero near 1.5GPa. These centers appear to be pair breaking, and in fact Howard et al. [5] have developed in some detail the idea of some intrinsic scattering being responsible for a considerable reduction in the \( T_C \) of CeCoIn$_5$, although not precisely along these lines.

A further experimental result consistent with this line of thinking is the observation by Stock et al. [6] of an inelastic neutron resonance that develops below \( T_C \) in CeCoIn$_5$. There is considerable weight in this resonance, and it can plausibly be thought that it comes from the gapping out of the residual Kondo centers in the superconductor present at \( T_C \). This explains as well the large specific heat jump at \( T_C \). The decrease in the the specific heat jump with pressure just corresponds to the decreasing concentration of these centers with pressure. In this simple picture then we have the antiferromagnetism arising in Cd-doped CeCoIn$_5$, for example, from the RKKY coupling of the Kondo centers that have not yet condensed into the heavy electron liquid. It is worth noting that in CeCoIn$_5$, the single ion Kondo temperature of Ce measured in LaCoIn$_5$ is 1.7K [7]. The proximity of CeCoIn$_5$ [5] to an antiferromagnetic quantum critical point has been demonstrated via Cd-doping experiments where small substitution of In by Cd generates a phase diagram versus Cd concentration which closely resembles that of CeRhIn$_5$ versus pressure.

This appears however not to be the whole story as far as heavy Fermion superconductivity in Ce-based materials is concerned. Experiments 9 on CeCu$_2$Si$_2$ Ge-doped CeCu$_2$Si$_2$ find two apparently separated domes of superconductivity suggesting the phase diagram of Fig. 5. The idea is that there is not only magnetically mediated superconductivity but superconductivity arising from charge fluctuations in an intermediate valence regime. Such a possibility goes back to Varma et al. [10] and was later developed in more detail by Holme et al. [11]. This calls to mind the superconductivity seen
at high pressure in $\alpha'$-Ce and the recent studies of its phonon spectrum via inelastic x-ray scattering [12]. In these it was seen that $\alpha'$-Ce is on the verge of a lattice instability and possibly a charge density wave instability, suggestive of its superconducting properties arising from this intermediate valence background.

So our question is then, do we see anything like this in 5f-based heavy Fermion superconductors? We first look at elemental U and Ube$_{13}$. Elemental U is not classed as a heavy Fermion superconductor, but it has some remarkable similarities to $\alpha'$-Ce discussed above. First, the superconducting phase $\alpha$-U has the same crystal structure, and it has as well a set of charge density wave instabilities that interfere with superconductivity. Full bulk superconductivity is only achieved in $\alpha$-U at pressure sufficient to quench the charge density waves [13]. Apparently it is not known at present whether a CDW can co-exist in superconducting $\alpha$-U at pressures where superconductivity occurs before any evidence of a CDW is seen. Nevertheless, $\alpha$-U appears a good candidate for charge fluctuation mediated superconductivity.

Ube$_{13}$, the first heavy Fermion superconductor identified after CeCu$_2$Si$_2$, bears close similarities to other heavy Fermion superconductors that would be classed as close to a quantum critical point and we note here some parallels with the properties of CeCoIn$_5$. The specific heat jump at $T_C$ is considerably larger than weak coupling BCS (Fig. 6) [14], but not nearly as large as in CeCoIn$_5$. There is also seen below $T_C$ the development of an inelastic neutron resonance, although with considerably less weight than that seen in CeCoIn$_5$ [15]. There is present a substantial negative magnetoresistance that
shows that the residual resistivity in the normal state depends strongly on magnetic field, a result that indicates a large intrinsic residual resistivity just as in CeCoIn$_5$ (Fig. 7) [16]. These features of UBe13 all show striking similarity to those of CeCoIn$_5$.

But UBe$_{13}$ has another life. When Th-doped, a second superconducting region of different nature appears, as strongly evidenced by the presence within it of two superconducting transitions. Further, when magnetic field is applied, the second superconducting region completely separates from the first, appearing very much like the schematic phase diagram in Fig. 8 [17]. However, that the second dome is coming from valence fluctuations seems unlikely, given the small variation in entropy recovered by $T_C$ in the various alloys. More likely seems the possibility that a changed Fermi surface topology underlies this unusual behavior.

The intensely studied heavy Fermion superconductor UPt$_3$ provides a strong case for belonging to a different class than CeCoIn$_5$ [18]. This material shows Fermi liquid properties at low temperature, with no obvious indication of being close to any magnetic quantum critical point. The entropy developed out to $T_C = 0.56$ K is small by heavy Fermion standards, approximately 0.04Rln2 and the specific heat jump at $T_C$ is slightly smaller than the weak coupling BCS, when allowance is made for the sizeable residual normal electron fraction at $T = 0$ K required by entropy balance. There are three different superconducting phases existing, two of them seen in zero applied magnetic field. It is believed that all these states have triplet pairing [19]. There are reasons as well for supposing that the 1.7 K superconductor U$_2$PtC$_2$ with somewhat smaller electronic specific heat $\gamma$ than UPt$_3$ may also fall into the charge fluctuation characterization.

The hexagonal UPd$_2$Al$_3$ [21] and UNi$_2$Al$_3$ [22] have antiferromagnetic order coexisting with a lower temperature superconductivity. Inelastic neutron scattering experiments [23] on UPd$_2$Al$_3$ show a strong renormalization of the inelastic response below the superconducting $T_C$, reminiscent of what was seen by Stock et al. in CeCoIn$_5$. The hidden order phase of URu$_2$Si$_2$ which also supports superconductivity well below the hidden order transition appears to be a unique material with properties which do not fit the pattern of other heavy Fermion systems [23]. There is as well the unusual ferromagnet URhGe [24] where superconductivity and ferromagnetism coexist, as they do similarly in the related ferromagnets UCoGe [25] and UGe$_2$ [26]. In the case of UCoGe, it is argued that a ferromagnetic quantum critical point exists under the dome of superconductivity in the temperature-pressure plane, but the different physics of this situation contains components that call for separate consideration.

The $T_C = 5.0$ K Np-based superconductor NpPd$_2$Al$_2$ (Fig. 9) [27] also appears in the class with CeCoIn$_5$. Not only is the large entropy of 0.15Rln2 developed by $T_C$, the specific heat jump at $T_C$ is also considerably larger than the weak coupling BCS limit. We see as well that the entropy balance requires approximately a doubling of the electronic specific heat $\gamma$ at $T = 0$ K. In this case $\Delta C/\gamma dT$ is very close to weak coupling BCS. The extra entropy that develops above the value of $\gamma T$ at $T_C$ is approximately 0.08Rln2, quite similar to that seen in CeCoIn$_5$.

In the case of the Pu-based superconductors, it has been suggested that the large $T_C = 18$ K of PuCoGa$_5$ may arise in a charge fluctuation dome, with the 2 K superconductor PuCoIn$_5$ being of the CeCoIn$_5$ antiferromagnetic quantum critical type. There is not enough specific heat data to really make a good comparison between the materials based on this, but the comparison of lattice volumes for the two in relation to the volumes of the corresponding rare earth materials is interesting and gives support to the idea that these two compounds may be in different regimes (Fig. 10) [28]. It is known that the actinide elements when their 5f’s become fully localized have volumes which lie close to those of the cor-

Fig. 8. $T_C$ of Th-doped UBe$_{13}$ as function of field and composition [17].

Fig. 9. (Color online) Specific heat divided by $T$ for NpPd$_2$Al$_2$ [27].
responding rare earth elements. One expects this then to be true as well for the corresponding intermetallic compounds and for Pu this means that if it has fully localized 5f5 configuration it will correspond with Sm. In Fig. 10 we see that PuCoIn5 and SmCoIn5 have identical volumes, while that of SmCoGa5 is considerably larger than that of PuCoGa5. That this difference is significant is further seen by the fact that PuCoGa5 has smaller volume than AmCoGa5, indicating that the actinide contraction which corresponds to the lanthanide contraction has not yet set in at Pu within the series. Assuming that AmCoGa5 is localized 5f6, the two points of SmCoGa5 and AmCoGa5 are approximately parallel to the line for the lanthanide contraction seen in the rare earth Co-In 115 sequence. This argument is quite suggestive of intermediate valence behavior in PuCoGa5.

It appears from the considerations above that the 4f and 5f superconductors fit into similar classification. The surprise then is that we have not found, for example, the 20 K Ce-based superconductor. It seems that it should be there.

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