UC Irvine

UC Irvine Previously Published Works

Title

Heavy fermion superconductivity: 5f vs 4f

Permalink

<https://escholarship.org/uc/item/1fv5025q>

Journal

Journal of the Korean Physical Society, 63(3)

ISSN

0374-4884

Authors

Fisk, Z
Haga, Y

Publication Date

2013-08-01

DOI

10.3938/jkps.63.795

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Heavy Fermion Superconductivity: 5f vs 4f

Zachary FISK*

*University of California, Irvine, California 92697, U.S.A. and
Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan*

Yoshinori HAGA

Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

(Received 6 June 2012)

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.

PACS numbers: 74.70.Tx, 71.27.+a, 72.15.Qm

Keywords: Heavy Fermion, Superconductivity

DOI: 10.3938/jkps.63.795

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 Fermion superconductors, nevertheless it is remarkable that the heavy Fermions are perhaps the only class of materials where we have some good idea where to look for superconductors.

A useful way to think about heavy Fermion materials is from the standpoint of the dense Kondo lattice. Chemically ordered Ce compounds in the heavy Fermion class can be regarded as a set of Kondo centers which condense at low temperature into a coherent heavy electron liquid. This condensation is characterized by a coherence temperature, quite generally visible as a peak in the temperature dependent electrical resistivity. This coherence temperature corresponds to an energy which sets the scale for the low temperature physics as out-

lined in Fig. 2. In many cases of interest the 4f¹ crystal field ground state of Ce is a doublet, and the essential problem the Ce intermetallics are dealing with at low temperature is shedding the associated $R\ln 2$ entropy per mole Ce. One way to quantify the coherence temperature is as that temperature by which this $R\ln 2$ entropy has evolved in the electronic system.

In the vicinity of an antiferromagnetic quantum critical point the specific heat typically varies as $T\ln(T^*/T)$ with coefficient of order $R\ln 2/T^*$, 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 θ 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 co-exist 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 CeCoIn₅ support this assertion. The entropy developed to T_C is approximately 0.15 $R\ln 2$ per Ce. At T_C ,

*E-mail: zfish@uci.edu

Fig. 1. (Color online) Temperature - pressure phase diagram of the pressure induced heavy Fermion superconductor CeRhIn₅ [1].

$$C/T \propto \ln T$$

$$\text{Typically: } C/T = (R \ln 2 / T^*) \ln(T^*/T) \\ \text{and } S(T^*) = R \ln 2$$

T* sets the scale for heavy Fermion physics

For heavy Fermion superconductors:

$$S(T_c) \sim 10\text{-}20\% R \ln 2 \leftrightarrow T_c/T^* \sim 1/20$$

Fig. 2. Entropy development in the dense Kondo lattice in the vicinity of an antiferromagnetic quantum critical point. C is the specific heat per mole f-element, S the entropy and T^* the coherence temperature.

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 ΔC , 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 1.5 GPa. 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 CeCoIn₅, 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

Fig. 3. Dependence of T_C and the specific heat jump on pressure in CeCoIn₅ [3].

CeCoIn₅. 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 CeCoIn₅, 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 CeCoIn₅, the single ion Kondo temperature of Ce measured in LaCoIn₅ is 1.7 K [7]. The proximity of CeCoIn₅ to an antiferromagnetic quantum critical point has been demonstrated via Cd-doping experiments [8] where small substitution of In by Cd generates a phase diagram versus Cd concentration which closely resembles that of CeRhIn₅ 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 CeCu₂Si₂ Ge-doped CeCu₂Si₂ 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

Fig. 4. (Color online) Pressure dependence of residual resistivity ρ_0 , coefficient of T power law resistivity and superconducting transition width in CeCoIn_5 [4].

Fig. 5. (Color online) Schematic of the two domes of superconductivity seen in CeCu_2Si_2 [9].

at high pressure in α' -Ce and the recent studies of its phonon spectrum via inelastic x-ray scattering [12]. In these it was seen that α' -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

Fig. 6. (Color online) Electronic specific heat divided by T versus T in UBe_{13} [14].

Fig. 7. Magnetic field dependence of the residual resistivity in UBe_{13} [16].

look at elemental U and UBe_{13} . Elemental U is not classed as a heavy Fermion superconductor, but it has some remarkable similarities to α' -Ce discussed above. First, the superconducting phase α -U has the same crystal structure, and it has as well a set of charge density waves that interfere with superconductivity. Full bulk superconductivity is only achieved in α -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 α -U at pressures where superconductivity occurs before any evidence of a CDW is seen. Nevertheless, α -U appears a good candidate for charge fluctuation mediated superconductivity.

UBe_{13} , the first heavy Fermion superconductor identified after CeCu_2Si_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

Fig. 8. T_C of Th-doped UBe₁₃ as function of field and composition [17].

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 CeCoIn₅ (Fig. 7) [16]. These features of UBe₁₃ all show striking similarity to those of CeCoIn₅.

But UBe₁₃ 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 UPt₃ provides a strong case for belonging to a different class than CeCoIn₅ [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 $0.04R\ln 2$ and the specific heat jump at T_C is slightly smaller than 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 U₂PtC₂ with somewhat smaller electronic specific heat γ than UPt₃ may also fall into the charge fluctuation characterization.²⁰

The hexagonal UPd₂Al₃ [21] and UNi₂Al₃ [22] have antiferromagnetic order coexisting with a lower temperature superconductivity. Inelastic neutron scattering experiments [23] on UPd₂Al₃ show a strong renormaliza-

Fig. 9. (Color online) Specific heat divided by T for NpPd₅Al₂ [27].

tion of the inelastic response below the superconducting T_C , reminiscent of what was seen by Stock *et al.* in CeCoIn₅. The hidden order phase of URu₂Si₂ 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 UGe₂ [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 NpPd₅Al₂ (Fig. 9) [27] also appears in the class with CeCoIn₅. Not only is the large entropy of $0.15R\ln 2$ 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 γ at $T = 0$ K. In this case $\Delta C / \int \gamma dT$ is very close to weak coupling BCS. The extra entropy that develops above the value of γT at T_C is approximately $0.08R\ln 2$, quite similar to that seen in CeCoIn₅.

In the case of the Pu-based superconductors, it has been suggested that the large $T_C = 18$ K of PuCoGa₅ may arise in a charge fluctuation dome, with the 2 K superconductor PuCoIn₅ being of the CeCoIn₅ 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. 10. (Color online) Comparison of unit cell volumes of rare earth and actinide 115s [28].

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.

REFERENCES

- [1] T. Park *et al.*, Proc. Natl. Acad. Sci. USA **105**, 6825 (2008).
- [2] C. Petrovic *et al.*, J. Phys.: Cond. Matter **13**, L337 (2001).
- [3] G. Sparn *et al.*, Physica B **319**, 262 (2002).
- [4] V. A. Sidorov *et al.*, Phys. Rev. Lett. **89**, 157004 (2002).
- [5] L. Howard *et al.*, New J. Phys. **13**, 113039 (2011).
- [6] C. Stock *et al.*, Phys. Rev. Lett. **100**, 087001 (2008).
- [7] S. Nakatsuji *et al.*, Phys. Rev. Lett. **89**, 106402 (2002).
- [8] L. D. Pham *et al.*, Phys. Rev. Lett. **97**, 056404 (2006).
- [9] H. Q. Yuan *et al.*, Science **302**, 2104 (2003).
- [10] C. M. Varma, S. Schmitt-Rink and E. Abrahams, Solid State Commun. **62**, 681 (1987).
- [11] A. T. Holmes, D. Jaccard and K. Miyake, J. Phys. Soc. Jpn. **76**, 051002 (2007).
- [12] I. Loa *et al.*, Phys. Rev. Lett. **108**, 045502 (2012).
- [13] C. W. Chu and G. S. Knapp, Phys. Lett. A **46**, 46 (1973).
- [14] H. R. Ott *et al.*, Phys. Rev. Lett. **50**, 1595 (1983).
- [15] A. Hiess, private communication.
- [16] U. Rauchschwalbe, F. Steglich and H. Rietschel, Europhys. Lett. **1**, 71 (1986).
- [17] S. E. Lambert *et al.*, Phys. Rev. Lett. **57**, 1619 (1986).
- [18] R. A. Fisher *et al.*, Phys. Rev. Lett. **62**, 1411 (1989).
- [19] Y. Machida *et al.*, Phys. Rev. Lett. **108**, 157002 (2012).
- [20] G. P. Meisner *et al.*, Phys. Rev. Lett. **53**, 1829 (1984).
- [21] C. Geibel *et al.*, Z. Phys. B **84**, 1 (1991).
- [22] C. Geibel *et al.*, Z. Phys. B **83**, 305 (1991).
- [23] T. T. M. Palstra *et al.*, Phys. Rev. Lett. **55**, 2727 (1985).
- [24] D. Aoki *et al.*, Nature **413**, 613 (2001).
- [25] S. S. Saxena *et al.*, Nature **406**, 587 (2000).
- [26] E. Slooten *et al.*, Phys. Rev. Lett. **103**, 097003 (2009).
- [27] D. Aoki *et al.*, J. Phys. Soc. Jpn. **77**, 159 (2008) Suppl. A.
- [28] E. D. Bauer *et al.*, J. Phys.: Condens. Matter **24**, 052206 (2012).