Non-cuprate Exotics, II: Heavy-fermions, Ruthenates, Organics

Heavy fermions[1]

The name "heavy-fermion system" is applied to a wide class of compounds containing rare-earth (usually Ce) or actinide (usually U) elements. The name comes from the fact that the electronic specific heat at low temperature exceeds that of standard textbook metals by a factor $\sim 100-1000$, indicating that (at least some of) the electrons have a very large effective mass (confirmed by e.g. dHvA measurements). These systems have different crystal structures (usually sc or hcp) but are all 3D rather than layered. Historically, the HF systems were the first to show superconductivity that is fairly clearly not of BCS type, and work on them has strongly affected thinking about the cuprates.

At temperatures $\sim$ R.T., the behavior of the HF systems is quite different from that of a textbook metal and not universal: cf. the behavior of $R(T)$, which is "metallic" for UPt_3 but "semiconducting" for UBe_{13}, $CeCu_2Si_2$ and $CeCu_6$ (see KK fig. 3.10). The magnetic susceptibility, however, is generally a decreasing function of T (roughly $\propto 1/T$), the nuclear relaxation rate $1/T_1$ is almost temperature-independent, $c_v^{\text{el}} \sim$const., and the neutron scattering data show a simple Lorentzian peak centered at $\boldsymbol{Q}=0$. All of these data appear compatible with a model in which the relevant electrons ($4f_1$ for Ce^{3+}, $5f_2$ for U^{4+}) form local moments on the individual lattice sites.

As the temperature is lowered, one usually crosses over to a "Fermi-liquid" regime,[2] characterized by the behavior $c_v \sim T$, $T_1^{-1} \sim T$, $\rho \sim \text{const} + T^2$ (electron-electron scattering). The point that distinguishes the HF systems is that the linear coefficient γ of the specific heat is enormous. In a simple textbook metal γ is of order mJ/mole K^2. However, among the HF's, γ in mJ/mole K^2 is: $CeCu_2Si_2$: 350, UPt_3: 400, $CeCu_2Si_2$: 1100, UBe_{13}: 1100, and $CeCu_6$ (the record-holder to date) 1600! Of course, it is not immediately clear that these enormous specific heats are associated with *mobile* electrons. However, confirmation that they are comes from the fact that for those of the above (all except $CeCu_6$) which become superconducting, the quantity $\Delta c_{n-s}/\gamma T_c$ is of the order of the BCS value 1.42. If we indeed interpret c_v this way, this implies that the DOS is a factor $\sim 10^3$ larger than for conventional metals: since the electron density and hence the "typical" value of k_{F} is comparable, this means that the effective mass must also be a factor $\sim 10^3$ times the free electron mass (hence, "heavy"). This interpretation is confirmed by measurements of the magnetic susceptibility, which is also a factor of $\sim 10^3$ greater than that of a typical textbook metal (so that the Wilson ratio ($\sim (1+F_a^0)^{-1}$ in the language of FL theory) is O(1); the large electron effective masses are also confirmed in dHvA measurements (the period of the oscillation measures the shape of the Fermi surface, and the temperature-dependence measures m^* (through the ratio $(\hbar eB/m^* k_{\text{B}} T)$).

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[1] Refs: Y. Kuramoto and Y. Kitaoka, Dynamics of Heavy Electrons, Clarendon Press, Oxford 2000: J-P. Brison et al., Physica B **280**, 165 (2000).

[2] In the case of UBe_{13} this regime is quite narrow (below $\sim 2.4K$, with $T_c \approx 0.9K$); in other HF systems it is larger compared to T_c.

A naïve picture of what is going on can be obtained if we assume that the $4f/5f$ electrons are in principle mobile but with a very small hopping matrix element (say $\lesssim 1K$). In a tight binding model the relevant states would then form a very narrow band with a width $\Delta \sim$ a few K., Then for $T \gtrsim \Delta$ we can equally well represent the system in terms of states *localized* on a given lattice site, and (for half-filling of the band) all the experimental properties will be the same as in such a model, e.g. χ will satisfy a Curie law ($\chi \propto 1/T$) and the electronic contribution to the specific heat will be small. That the "heavy" masses are indeed associated with the $4f(5f)$ shell is shown convincingly by the fact that in the alloy $Ce_xLa_{1-x}Cu_6$ the large low-temperature specific heat susceptibility are directly proportional to x. However, the above picture is much too naïve, because of the presence beside the $4f$ electrons of "conduction" (s- or d-band) electrons. In fact, much of the theoretical analysis of HF systems has been based on the idea of a "Kondo lattice."

In some cases, on the way between the high-T "pseudo-localized" state and the low-temperature FL-like one, the system undergoes an antiferromagnetic transition. We shall be particularly interested in the cases of $UPdAl_3$ ($T_N = 14.5$K, ordered moment 0.86 μ_B/atom) $UNiAl_3$ ($T_N = 4.6$K, moment 0.24 μ_B/atom) and URu_2Si_2, which is usually described as a "weak" antiferromagnet (although T_N is high, 17.5 K, the ordered moment per atom is very small, $\sim 0.04\mu_B$). Even those HF that do not become AF develop strong magnetic AF-type correlations (see in neutron scattering as T falls, and in the case of $CeRu_2Si_2$ there is a "pseudo-metamagnetic" transition at low temperatures at a field of $\sim$ 7T where the magnetization increases very steeply as a function of field. (A similar transition is seen in UPt_3 at $\sim$ 20T.) The general belief is that the details of the low-T behavior in the various HF systems is determined by the competition between the Kondo effect (which favors the formation of a singlet state between the (quasi-) localized f-electrons and the conduction electrons) and the RKKY interaction, itself an effect induced by the conduction electrons, which favors magnetic ordering and thus finite magnetic moments on the f-electrons. The problem is sufficiently complicated that whole books have been devoted to it (cf. KK); I will not discuss it further here.

There appears to be a close connection between the AF correlations and the heavy fermion masses; in particular, if the pressure is varied so as to bring the system close to or through an AF transition, the linear specific heat coefficient often increases as the transition is approached. This is further evidence that a simple tight binding band model is not the whole story.

Superconductivity in the heavy-fermion system

Superconductivity occurs in a number of HF compounds, but T_c, is never (much) above 2 K. The HF superconductors can be grouped into two classes: one, containing $CeCu_2Si_2$, UBe_{13} and UPt_3, has no other low-temperature phase transition. However, remarkably, there exists a second class in which superconductivity coexists with AF order: URu_2Si_2, $UNiAl_3$ and UPd_2Al_3. Generally speaking, the Sommerfeld coefficient is higher in the first class ($\gtrsim$ 400 mJ/mole K^2 versus $\sim$ 100 mJ/mole K^2), but the T_c's are opposite ($\lesssim 1K$ for first class, up to 2K in the second). In all cases $\Delta c_{n-s}/\gamma T_c \sim 1$, showing that it is indeed the "heavy" electrons that are (at least partly) responsible for the superconductivity.

It is necessary to discuss the different HF superconductors separately:

UPt_3 (hcp, paramagnetic, $T_c = 0.56$K)

UPt_3 is remarkable in that it possesses not one but three different ordered phases, all of which are superconducting (see KK fig. 5.8: note that phase diagram is topologically identical for $B \parallel c$ and $B \perp c$)[3]; the corresponding transition lines are observed in ultrasound attenuation, specific heat, magnetocaloric data ..., and appear all to correspond to *second-order* transitions (?), and no structural or magnetic phase transition has been seen. Note in particular the existence of a "tetracritical point."

Symmetry of pairing state:[4], the thermal conductivity is definitely entirely electronic in origin at temperatures $\lesssim T_c$, and explicitly is of the form $\kappa/T \propto a + bT^2$ for both c and ab-plane, where a is small. This strongly supports the existence of (non-"accidental") nodes in the OP both in the c-direction and in the ab-plane (also supported by $\sqrt{H}$ dependence of κ, due to vortices (?)).

In addition, strong evidence for odd-parity ($\approx$ spin-triplet) pairing comes from both H_{c2} and the Knight shift, though the two are not obviously mutually consistent: the Knight shift is essentially unchanged below T_c for *all* directions of field, indicating that the pair can re-orient. On the other hand, H_{c2} exceeds the CC limit in the basal plane but not along the c-axis, which would suggest a **d**-vector along the c-axis.

It seems very improbable that the occurrence of two different phases in zero field is just an accident: suggests rather that these arise from a 2- (or more) dimensional representation of the symmetry group of the hexagonal crystal, and that the degeneracy is broken, e.g. by coupling to AF fluctuations. Possibly E_{2u}?

[Mechanism: see below]

[Note: Magnetic + nonmagnetic scatterers appear to have roughly similar effect on T_c, also indicating odd-parity pairing.] (Dalichaouch et al., PRL **75**, 3938 (1995)).

$CeCu_2Si_2$ (simple cubic, paramagnetic, $T_c = 0.65$K)

Like UPt_3, $CeCu_2Si_2$ has several different low-temperature phases (see KK fig. 4.7), though in this case only one of them is superconducting. The A phase *may* be weakly AF.

Symmetry of the OP: The Knight shift appears reduced (to ~ 0.3 of the N-state value) independently of the direction of **B**, which suggests a spin singlet state. However, $T_1^{-1} \propto T^3$ at $T \ll T_c$, suggesting line nodes, while $c_v \sim T^3$, suggesting point nodes! $H_{c2}(\sim 1.3\text{T})$ does not appear to be anomalously large. So, everything consistent with spin singlet (even-parity) state with nodes.

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[3] The c-axis is defined as that normal to the hcp basal plane.

[4] Presumably the low-T statements refer to the B phase.

$\mathbf{UBe_{13}}$ (simple cubic, paramagnetic, $\mathbf{T_c = 0.9K}$)[5]

H_{c2} is large ($\sim$ 9T), probably above the Pauli limit, suggesting spin triplet (odd-parity) pairing. At low T, $c_v(T)$ and $T_1^{-1}(T)$ both $\propto T^3$, suggesting point and line nodes respectively (USA and $\lambda(T)$ measurements also show power law behavior.) A further piece of evidence comes from the mixed compound $U_{1-x}Th_xBe_{13}$, which in the range $0.02 - 0.04$ of x shows *two* transitions in the specific heat data.

$\mathbf{UPdAl_3}$ (hcp, AF, $\mathbf{T_c = 2K}$)

This compound goes AF on cooling at 14.5K, then S at 2K without any apparent modification of the magnetic order. The Knight shift decreases below T_c but only by $\sim 0.1\%$. However, this is probably not evidence for spin triplet pairing, because there is independent evidence (from a comparison of the N-state Knight shift with the known χ) that itinerant electrons anyway contribute only $\sim 0.1\%$. Hence the small decrease may in fact be regarded as evidence for *singlet* pairing! The value of H_{c2} is moreover compatible with Pauli limiting. Further evidence for spin singlet pairing comes from the observation of a Josephson effect with In.

Gap symmetry: the specific heat $\propto aT + bT^3$, where the aT term may be attributed to localized excitations (?). The T^3 would then point to *point* nodes, on the other hand, $T_1^{-1} \propto T^3$ at $T \ll T_c$ indicating line nodes. A further complication is that tunneling $\parallel$ c-axis shows a BCS-like I-V characteristic, with small subgap weight, indicating no nodes in this direction. It is not clear that there is *any* symmetry assignment that is consistent with all these pieces of data.

Summary on pairing states: $CeCu_2Si_2$ and $UPdAl_3$ are almost certainly even-parity, UBe_{13} and UPt_3 odd-parity, but all appear to have nodes in the gap at least in the ab-plane + possibly along the c-axis. U Ru_2Si_2 is a mystery ("hidden" OP).

$\mathbf{Sr_2RuO_4}$[6]

This is the newest of the exotic superconductors; indeed one reason for its intensive investigation over the last few years is that it is the only known superconducting layered perovskite not containing Cu (it is in fact isostructural to the parent compound LSCO, La_2CuO_4.)

At temperatures $\sim$ R.T., Sr_2RuO_4 is not typically metallic in its behavior, but for $T \lesssim 25$K in the N phase, it appears to behave as a highly anisotropic Fermi liquid. The specific heat is $\gamma T + \mathcal{O}(T^3)$, with $\gamma \sim 375$ mJ/mole K^2 (intermediate between conventional metals and HF's) χ is $\sim$ const $\sim 9 \times 10^{-3}$ emu/mole, giving an (average, see below) Wilson ratio of $\sim 1 - 2$. The electrical resistivity is $\sim T^2$ both in and out of

[5] Note that UBe_{13} differs from most of the other HF systems in having a very low value of the "coherence temperature."

[6] Mackenzie & Maeno (RMP **75**, 657) 2003.

plane: $\rho_{ab}/T^2 \sim 4.5 - 7.5\,\text{n}\Omega K^{-2}$, $\rho_c/T^2 \sim 4 - 7\ \ \mu\Omega\text{K}^{-2}$, so $\rho_c/\rho_{ab} \sim 10^3$ (similar to cuprates in magnitude though not in T-dependence).

DHvA measurements show 3 peaks in the amplitude spectrum as a function of B, which have been assigned to 3 nearly cylindrical Fermi surfaces, two (α, β) electron-like and one (γ) hole-like; these are thought to be hybridized Ru($4d$)-O($2p$) bands. The m^*/m ratio is respectively 3.4(α), 7.5(β) and 14.6(γ), (in agreement with the specific heat data).[7]

Thus, the normal state at $T \gtrsim T_c$ appears rather well understood.

T_c for the present samples is 1.5K.

It seems almost certain that the pairing state is non-s-wave, and very probable that it is spin triplet (odd-parity). Evidence:

1. T_c is extremely sensitive to nonmagnetic impurities such as Al (a mean free path as long as 10^3Å is sufficient to destroy superconductivity altogether) $\Rightarrow$ not s-wave.

2. The Knight shift for H in the ab-plane is unchanged from the normal state (at least down to 15mK) $\Rightarrow$ spin triplet. (c-axis?)

3. T_1^{-1} shows no HS peak, and below 0.7K $1/(T_1 T) = \text{const} \Rightarrow$ spin triplet.

4. The specific heat shows a large residual DOS for $T < T_c$.

5. Josephson experiments similar to those on cuprates (Kim et al., JLTP **131**, 1059, 2003) $\Rightarrow$ OP changes sign on reflection (i.e. odd parity).

6. The most direct evidence for breaking of T-reversal symmetry comes from the observations in μSR of a *spontaneously generated magnetic field* in the superconducting state (Uemura et al., Nature **394**, 558 (1998).

7. More recent Josephson-type experiments (Kidwingira et al., Science **314**, 2167 (2006)) consistent with breaking of T-reversal symmetry in domains.

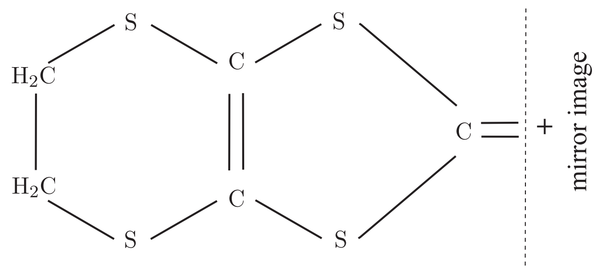
A symmetry assignment which until recently seemed to cope with all the above data is $\mathbf{d} = \hat{z}(k_x + ik_y)$ (i.e. spins in ab-plane, orbital angular momentum $l = 1$ along c-axis). Such a state would possess only point nodes in the directions $\pm\hat{z}$ and in particular would have no nodes in the ab-plane. However ...

Mechanism: at first sight, plausible to suspect FM-like spin fluctuations. However, (average) Wilson ratio is only $\sim 1.5 - 2$: compare $6 - 8$ for Pd, 12 for Ti Be_2, 40 for Ni_3Ga. Also χ is not as T-dependent nor c_v so H-dependent as in those compounds. Nevertheless...

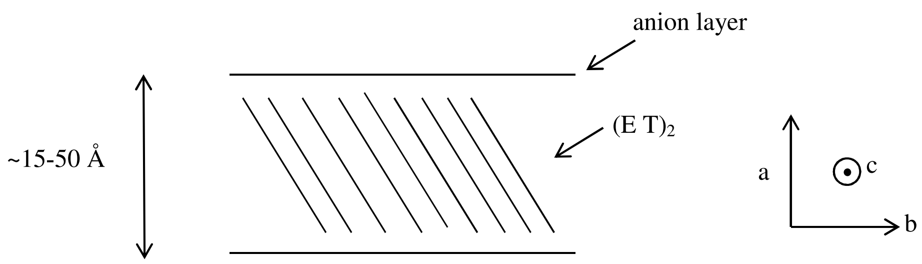
[7] Wilson ratio is said to be 2.2 for α, β, 1.2 for γ.

Organics:*

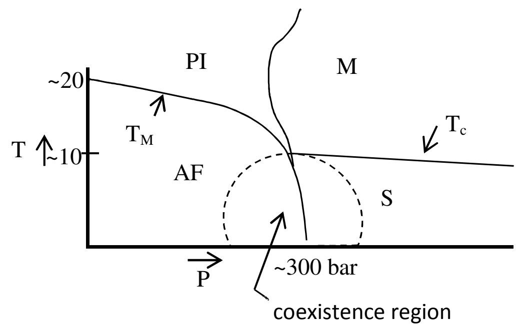
Most organic superconductors are quasi-2D crystals based on bis(ethylene-dithio)-tetrathiofulvalene -TFF ⇒ BEDT-TFF ⇒ ET



They are charge-transfer salts with structure (usually) $(ET)_2X$, where X is a monovalent anion, e.g. I_3^-, $Cu(NCS)_2^-$, etc. The general structure is



where, confusingly, the axis perpendicular to the planes is conventionally labelled *a* rather than *c*. The actual arrangement of the ET molecules depends on the particular anion, but generally speaking it is reasonably "isotropic" in the bc-plane. The generic phase diagram of (most of) the organics in the P=T plane is roughly



*A very readable reference is J. Singleton and C. Mielke, Contemporary Physics **43**, 63 (2002). For a more extended discussion, see T. Ishiguro et. al., Organic Superconductors, Springer, Berlin 1994 (but by now somewhat out of date).

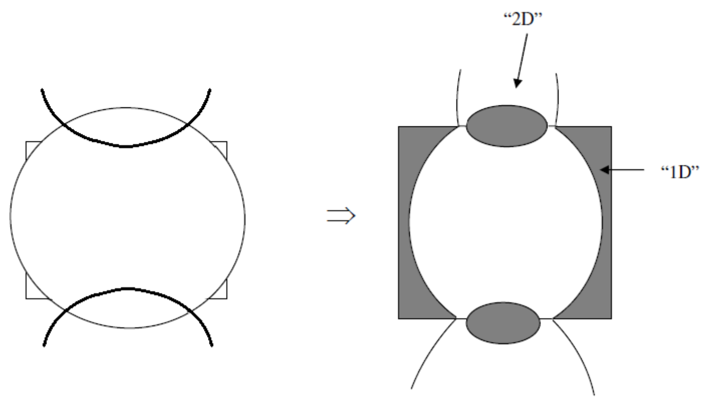
The insulator→ metal transition presumably does not involve the electrons which are donated to the anions, but rather the holes they leave on the $(ET)_2$'s. In the M(or S) phase the conduction electron density is $\sim 10^{21}$ cm$^{-3)}$, comparable to the cuprates. The anisotropy of the N-state (M) resistivity is small in the bc-plane but very large along the c-axis ($\rho_a/\rho_{bc} \sim 10^3 - 10^5$, comparable to cuprates). The organic superconductors are often believed to be "cousins" of the cuprates (and ferropnictides) because

(a) they are strongly 2-dimensional

(b) superconductivity occurs close to an AF state

(c) despite the small absolute value of T_c (typically 10-12 K), when this is scaled by the theoretically estimated in-plane hopping matrix element ($t_{||} \sim 150$ meV) they are "high-temperature" superconductors.

However, it turns out that it is much easier to determine the band structure etc. than for the cuprates (this is partially because they can be made very "clean", mfp in N state ~ 2000 $\AA$). Band structure: (in plane, κ-type)



(β-type OS's have a single (closed) hole-like FS). Very surprisingly, magnetoresistance experiments strongly suggest that even though $t_\perp$ (hopping ME normal to planes) is estimated to be only $\sim$0.04 meV, hence $\ll k_BT$, band structure is 3-dimensional. (See Singleton & Mielke for detailed discussion.)

Normal state: somewhat conventional, $\rho_{bc}(T) \sim T^2$ at least up to $\sim$30-40K, thereafter complicated, (similar to (some) HF systems)

S state: Superconductivity is extreme type-II: $B_{c1} \sim$ a few mT for B $\parallel$ plane, $B_{c2}(0) \sim 8 - 15$T (but considerable irreversibility): At yet higher fields system may become *insulating*. Estimated $\xi_{||}(0) \sim 50$Å, $\xi_\perp(0) \sim 5$Å (< interlayer distance, ~ 50Å).

Mechanism:

(a) Isotope effect: the substitution $^{12}C \rightarrow {}^{13}C$ reduces T_c, as does $^{32}S \rightarrow {}^{34}S$, in qualitative agreement with BCS. Effect of deuteration ($^1H \rightarrow {}^2H$ for all ethylene H's) more complicated: in $\kappa-(ET)_2$ $Cu(N(CN)_2)Br$ gives large isotope effect with "normal" sign (i.e. $T \downarrow$) but in $\kappa-(ET)_2$ $Cu(NCS)_2$ a large *inverse* isotope effect–thought to be due to different effects of lattice deformation. The situation is complicated by the fact that there is also an appreciable isotope effect on the magnetic properties (T_N); thus the effect on T_c could be indirect, via the spin fluctuations. Further evidence in favor of phonon mechanism: below T_c shift in the energy of phonons with $\omega \sim 2\Delta$ seen in neutron scattering, also hardening of phonon modes seen in Raman. $\Delta c_v/\gamma T_c \cong 2.1$, typical of strong-coupling phonon superconductors.

(b) Symmetry of the order parameter: the evidence on this appears to be mutually somewhat inconsistent. The low-T specific heat is exponential, with no hint of a power-law tail,[8] but the low-T $T_1^{-1} \propto T^3$ (de Soto et al.) and there appears to be no HS peak. Note also the existence of the quasi-1D organic superconductor $(TMTSF)_2$ PF_6, where in one direction H_{c2} exceeds CC limit by a factor ~ 3 ($\Rightarrow$ triplet pairing?) Singleton and Mielke conclude that most evidence other than the specific heat points to a d-wave gap, and that the pairing mechanism is probably some combination of electron-phonon and electron-electron (e.g. spin-fluctuation) effects.

[8] However, see Nakazawa et al., Physica **282**C, 1817 (1997). Thermal conductivity also appears to be power-law. $\lambda(T)$: Carrington et al. (PRL **83**, 4172 (1999)) find $\Delta\lambda(T) \propto (T/T_c)^{3/2}$ in $\kappa-(ET)_2$ - $Cu[N(CN)_2]Br$ and $\kappa-(ET)_2$ - $Cu(NCS)_2$ from $T/T_c \sim 0.01$ to ~ 0.1. Also find $\lambda_\perp^{-2}(T) \sim \lambda_\perp^{-2}(0)(1 - \beta T^n)$, $n = 1.2 \pm 0.1$, with $\lambda_\perp(0) = 100 \pm 20\mu$ (comparable to Bi-2212).