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# Searching for heavy fermion materials

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**Abstract**

Some history from a personal viewpoint is given of materials-driven heavy Fermion physics.

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My introduction to Kondo physics came as a graduate student of Bernd Matthias. In 1958, rare earths of good purity had become available and as part of his effort to understand what mattered in superconductivity, Matthias looked at the effect of rare earth additions on the superconducting transition temperature of FCC La [1]. Suhl explained the general pair breaking variation with J.s, but Ce impurities clearly had an anomalously large effect. Sugawara and Eguchi (1966) [2] subsequently showed that Ce dissolved in La was a Kondo center, displaying a log T temperature-dependent electrical resistivity at low temperatures that had been recently proposed by Kondo (1964) [3]. Matthias' student Brian Maple was engaged in a study (1966) of the effect of rare earth impurities on the 3.2 K $T_c$ of $LaAl_2$ [4], and, as in elemental La, the effect of Ce on $T_c$ was unexpectedly large. This led Brian to the idea that Ce dissolved in $LaAl_2$ was also a Kondo ion. Brian asked me to measure the electrical resistance of these alloys, confirming the Kondo effect here. I undertook a similar study of rare earth substitutions on the 7 K $T_c$ of $YB_6$, finding yet again that Ce was here a Kondo center [5] (Fig. 1). Almost immediately we realized that the pure compounds $CeAl_2$ and $CeB_6$ displayed in their resistivities strong Kondo features, and that somehow the Kondo physics was playing out in the dense, chemically ordered lattice as well. It was not really appreciated until the mid-1970s with the experiments on $CeAl_3$ [6] just how strongly conduction electrons near the Fermi surface were renormalized in such materials. It is interesting that a decade and an half later, Allen and Martin [7] provided a Kondo impurity explanation for the mysterious isostructural $\gamma$–$\alpha$ transition in elemental Ce, a model which predicted a closed-loop first-order region—analogous to a miscibility gap—in the pressure–temperature diagram of CeLaTh alloys which was subsequently found [8].

Kondo physics suddenly changed in 1979 with the astonishing discovery of superconductivity in $CeCu_2Si_2$ by Steglich [9]. Ce-based superconductors were known at that time but seemed unexceptional in their normal-state properties. Also known were the re-entrant materials (e.g., rare earth moly sufides and rhodium tetraborides) with their competing magnetic and superconducting order. But now one had a superconductor whose normal state properties had strong magnetic parentage and whose specific heat anomaly at $T_c$ indicated that the superconducting gap was opening in a very high density of states band. Moreover, this result dispelled any doubt as to any other than electronic origin of the enormous electronic specific heat $\gamma$ in $CeAl_3$. The search was then on in earnest for new superconductors in this class as well as other unusual phenomena in these high $\gamma$ materials. Low-temperature specific heat became the diagnostic of choice.

But new Ce superconductors in this class were not immediately forthcoming. I had moved to Los Alamos following the death of Matthias in 1980 and had been developing metallic flux techniques for the growth of f-element intermetallics. Hans Ott, whom I had collaborated with on hexaboride projects remembered a paper of

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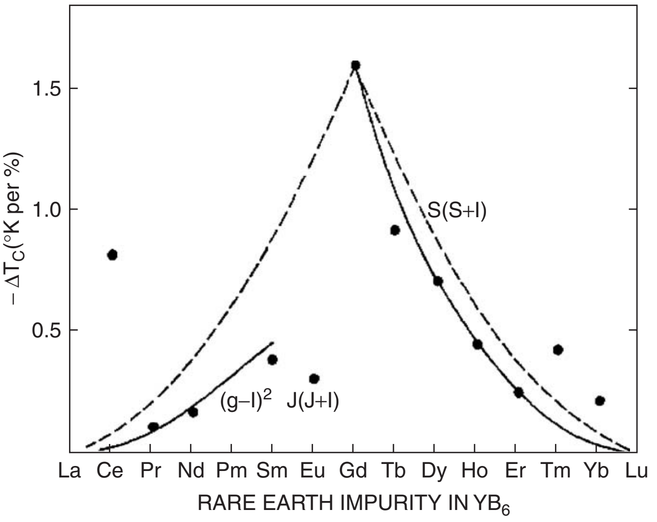

Fig. 1. Depression of $T_c$ of $YB_6$ by rare-earth impurities [5].

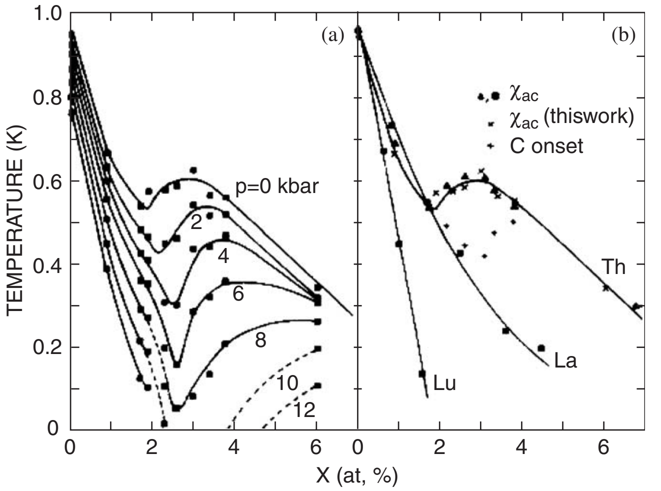

Fig. 2. (a) Effect of pressure on $T_c$ of Th-doped $UBe_{13}$. (b) depression of $T_c$ of $UBe_{13}$ by Lu, La and Th [14].

Ernst Bucher on $UBe_{13}$ in which superconductivity had been observed near 1 K, but Bucher had convinced himself that it was of filamentary nature [10]. Ott believed that it was perhaps a uranium version of the Ce-type heavy Fermion superconductivity, but that nobody would believe the result if it was not demonstrated in single crystal material. My experience suggested that Al should be a suitable flux for the growth of $UBe_{13}$, and large crystals proved straightforward to grow, once I realized that BeO, the crucible material I was using, soaked up large amounts of moisture even in New Mexico and needed to be baked out before use. The electrical resistivity of the material had interesting similarities to that of $CeCu_2Si_2$ and the low-temperature specific heat immediately confirmed bulk, strong coupling superconductivity at 0.9 K [11].

The low-temperature electronic specific heat $\gamma$ of 1 J/mol-UK$^2$ indicative of highly correlated electrons at the Fermi surface suggested the possibility of non-s-state pairing, something that had been looked for and not found in Pd [12]. The signature for this was found in power-law rather than exponential T-dependence of various properties below $T_c$ [13]. Equally indicative signature was found through the dependence of $T_c$ with doping on the U-site [14]. Not only was there no strong dependence on the presence of a magnetic moment on the dopant atom, Th-doping had strong nonmonotonic effect on $T_c$ (Fig. 2). Specific heat measurements in the Th concentration range of nonmonotonic behavior found two bulk superconducting transitions [15], strongly suggesting a nontrivial superconducting order parameter in $U(Th)Be_{13}$.

The possibility of strong parallels between 4f and 5f materials came immediately to the fore. It was known that $UPt_3$ crystallized in the same hexagonal structure as the original heavy Fermion material $CeAl_3$, prompting an attempt to grow crystals of this material. Nice needles grew from Bi-flux, and these has a residual resistance ratio to 1 K of over 100, suggesting that deHaas–van Alphen might be possible. Checking the resistance to lower $T$ discovered their superconductivity near 0.5 K. The specific heat measured on these by Stewart showed a somewhat rounded anomaly corresponding to $T_c$, holding up acceptance of the subsequent paper by PRL [16]. This rounded feature was later shown to be hiding a double superconducting transition, evidence of another non-trivial superconducting order parameter [17].

As with Ce-based materials, many U intermetallics appeared to develop large electronic specific heats at low temperature which were unstable against magnetic order, the antiferromagnets $U_2Zn_{17}$ [18] and $UCu_5$ [19], for example. What was different in the case of the U intermetallics was that the residual $\gamma$ in the ordered state did not go to a low value as with the typical Ce magnetically ordered heavy Fermions, rather only about 2/3 of the pre-ordering $\gamma$ was lost. In the case of $U_2Zn_{17}$ Aeppli and collaborators found that the square of the ratio of the ordered moment to the paramagnetic moment was this number 2/3, providing a rationalization for the residual $\gamma/3$ [20]. A further feature characteristic of the magnetic order in the U heavy Fermions is that the integrated entropy to $T_N$ is smaller, 20% smaller typically, than the entropy $S = \gamma_{Tn} T_N$, namely the entropy one supposes should be residing in the heavy Fermion electronic state at $T_N$, indicating that a BCS-type description such as given by Fedders and Martin for Cr [21] does not work in a simple way here.

The question arose as to whether this residual large $\gamma$ so often found could itself be unstable against further order. In the case of $UCu_5$, samples with sufficiently high resistance ratios did in fact undergo a further phase transition near 1 K [19] (Fig. 3), well below the $T_N = 15$ K higher temperature antiferromagnetic transition. The exact nature of this low temperature is not known, and involves an increase in the electrical resistivity of nearly an order of magnitude.

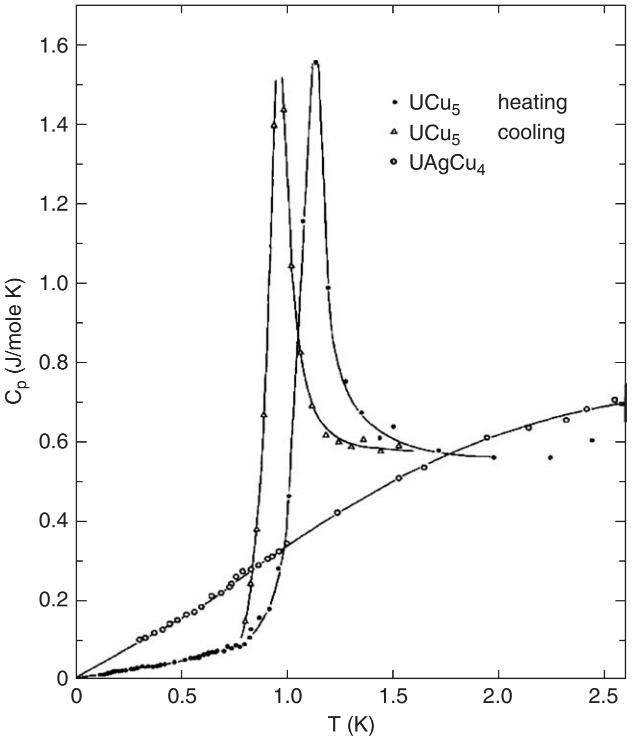

Fig. 3. Specific heat anomaly at low-temperature phase transition within antiferromagnetically ordered $UCu_5$ [19].

The $ThCr_2Si_2$ structure of $CeCu_2Si_2$ is a remarkably common one for intermetallics, and much effort has gone into examining the Ce, Eu and Yb materials found in it. It was known since the early studies on the effect of pressure on the superconducting transition in La(Ce) by Maple [22] that pressure was an excellent knob for tuning the Kondo scale in materials, and the phase space for exploring for unusual properties was enormously expanded via pressure studies in Ce-based $ThCr_2Si_2$structure intermetallics. The interesting picture that slowly emerged from these studies was that heavy Fermion superconductors were found, perhaps even only found, very near the point where $T_N \rightarrow 0$ K, the so-called quantum critical point. This discovery changed dramatically the focus of heavy Fermion studies. In particular, Ce-based antiferromagnetic materials which develop entropy up to $T_N$ of much less than $R \ln 2$ become strong candidates for pressure-induced superconductivity. This lead to the discovery of Superconductivity beyond 1.8 GPa in $CeRhIn_5$ (Rh 115) [23], and the subsequent finding of the heavy Fermion superconductors $CeIrIn_5$ [24] and $CeCoIn_5$ [25]. The Co member here has been found to be remarkably suitable for detailed studies, very high-quality single crystals being quite easily produced. Its Fermi surface is known in some detail, showing some quite 2D pieces [26]. The energy scales of crystal field splitting and single ion Kondo temperature are two orders of magnitude different here, and a remarkably simple two fluid phenomenological model [27] can describe the development of the heavy electron state from the high-temperature-independent Kondo centers. The picture that emerges is one of a condensation of the Kondo centers below a lattice Kondo scale arising from Ce–Ce interactions. This lattice scale is essentially the so-called coherence temperature below which the electrical resistivity due to scattering off the Kondo centers disappears. In this picture, the establishment of coherence is exactly the loss of Kondo scattering, and the coherent heavy electron low-temperature state that develops incorporates the f's within its Fermi surface.

An unusual aspect of a small group of heavy Fermion U intermetallics is the co-existence of magnetic order with superconductivity. $URu_2Si_2$, discovered shortly after $UBe_{13}$, was the first found showing this, followed much more recently by the hexagonal $UNi_2Al_3$ [28] and $UPd_2Al_3$ [29]. This co-existence of magnetic and superconducting order was not found in Ce-materials until alloys between the 115 superconductors were studied [30].

The 4f-hole analog of Ce is Yb, and various Yb materials do show dense, Kondo lattice behavior. One interesting material is the C15b material $YbInCu_4$ discovered by Felner and Nowick [31]. The compound has an isostructural phase transition at 42 K, bearing strong similarities to the $\gamma$–$\alpha$ transition in elemental Ce. In particular, the phase transition in $YbInCu_4$ can be suppressed in magnetic field, and a model of Dzero and Gor'kov [32] based on free energy differences coming from the entropy of the $4f^{13}$ Hund's Rule ground state can describe the shape and g-factor of the suppression curve. Remarkably, an exactly similar magnetic field dependence is found for Ce alloys in magnetic field, where the $\gamma$–$\alpha$ transition has been reduced to temperatures more accessible to achievable magnetic fields [33].

Pressure has the opposite effect in Yb materials from that in Ce ones. This does not prevent one from accessing the quantum critical point going in the opposite direction with applied pressure, and many studies have been made to look for superconductivity in Yb-based intermetallics, so far without success. Applied magnetic fields can be used to suppress Néel temperatures, and these studies in many cases appear drive materials to quantum criticality and associated non-Fermi liquid behavior, but again no superconductivity has been found in Yb-based materials via this route.

A central issue remains the one that initially drove all the interest in the field: from where comes the superconductivity now seen to reside at the delocalization boundary? Can we say, further, that the establishment of coherence is in fact the development of a large Fermi surface? And does the full range of 4f correlated electron behavior cover the same phase space as that of the 5f's?

Matthias showed his students the virtue of having strong collaborations, a lesson I learnt well from him. I am grateful to him for this, as I am to my collaborators, so many of whom I have been working with for 20 years or more.

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