On the existence of heavy fermion ytterbium compounds*

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Abstract

Evidence for heavy fermion behavior in ytterbium compounds is examined.

1. Introduction

Heavy fermion materials are atomically ordered metals identified by a low temperature electronic specific heat coefficient γ two to three orders of magnitude larger than that of copper, for which $\gamma \approx 1$ mJ mol^{-1} K^{-2} [1–3]. The source of this large value for γ arises from the compensation of the magnetic moment associated with a nearly localized electron state, generally of f character, by the spins of the conduction electrons in the metal. The physics of this situation is generally believed to be closely related to Kondo impurity spin compensation, and indeed, many of the properties of the heavy spin fermion materials are those of a concentrated Kondo system [4]. However, at low temperature, below a characteristic or coherence temperature T^* of the given material (of the order of a typical Kondo temperature), the properties of these materials become those of a Fermi liquid with coherent Bloch states, albeit a Fermi liquid with a Fermi temperature of the order of this coherence temperature. A simple physical argument gives the magnitude of $\gamma \approx R \ln D / T^*$, where D is the degeneracy of the compensated f moment (usually two).

2. Heavy fermion cerium and uranium compounds

The most complete studies of heavy fermion materials are of those formed with the elements cerium and uranium. We know from lattice parameter considerations that the f moments of these elements in their heavy fermion

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compounds are quite localized. This means that the physics of the f electron materials can be described as one dominated by spin fluctuations. In cases where the f shell is less localized, as evident for cerium compounds in the deviation of the lattice parameters from the smooth trend of the lanthanide contraction, the situation is referred to as mixed valent, and charge fluctuations are now mixed with the spin fluctuations [5, 6]. This is inherently a more complicated situation, but the heavy fermion properties evolve smoothly into those of the mixed valent materials. The mixed valent situation is partially characterized by a larger Kondo scale (typically an order of magnitude larger than the heavy fermion scale), and one can think of the completely delocalized f limit as that of $T_K \to \infty$ [7].

In the case of cerium compounds we are dealing with an f^1 configuration. Whether or not the compound becomes a heavy fermion material depends on the other elements in the compound and their spatial arrangement with respect to the cerium atoms. The first coordination sphere of ligands around each cerium atom in the compound appears to determine to a large extent the f behavior, although we have very little ability to predict this behavior. Compounds of cerium are known covering the entire range from fully localized f without Kondo interactions, to heavy fermion, to mixed valent, to fully delocalized. Application of external pressure works in the direction of delocalizing the f electron of cerium, and this aspect has been investigated in many experiments [8–10].

Much of the interesting physics of heavy fermion materials derives from the low effective Fermi temperature T_F, which is of order of magnitude 1–10 K. As do transition metal compounds, heavy fermion materials display a variety of low temperature ground states: superconducting, magnetic or Fermi liquid. The proximity of the Fermi energy to the energy scale characterizing the superconducting and magnetic interactions suggests the viewpoint that these phase transitions are effectively strong coupling, "high" temperature phenomena, but ones which can be studied in the rather peaceful low temperature environment. It must be admitted that we really do not understand much in other than a qualitative way about the development of the low temperature coherent state, and it is for this reason that it is important to compare the heavy fermion properties exhibited by different f atom materials.

3. Ytterbium compounds

A particularly important element for comparison with cerium is ytterbium, the f^{13}, f hole analogue of f^1 Ce. In principle, the Kondo effect should be symmetrical between electrons and holes. This means that we should be able to display a set of ytterbium compounds whose low temperature electronic properties show the same range as those of known cerium compounds. In particular, we should be able to find heavy fermion compounds formed by ytterbium. It is our purpose in this paper to examine the evidence for this.

Unlike cerium, ytterbium as a dilute metallic impurity rarely appears as a Kondo ion. The case we have seen reported is for ytterbium in Ag–Au

alloys [11, 12]. There are a number of instances reported in intermetallic compounds, however [5] where good evidence for Kondo-type interactions is found. This is seen in the electrical resistivity ρ of such materials as YbAgCu$_4$ [13] and YbNiSn [14], for example. This is illustrated in Fig. 1, in which are shown ρ vs. temperature T data for YbXCu$_4$ compounds with X=Pd, Au and Ag [13]. The maxima at 1.1 K for X=Au and at 0.7 K for X=Pd are associated with freezing-out of magnetic scattering due to the onset of magnetic order. Evidence is also found in quasi-elastic neutron-scattering linewidths, for example, in YbBe$_{13}$ [15] and YbAl$_3$ [16]. In addition, there are a number of cases reported of ytterbium compounds with low temperature specific heats γ in excess of 100 mJ (mol Yb)$^{-1}$ K^{-2} (see Table 1). This body of data is good support for the claim that ytterbium acts as a Kondo-type ion in a number of its intermetallic compounds.

The two materials YbCuAl [17] and YbAgCu$_4$ [13] with $\gamma \approx 250$ mJ (mol Yb)$^{-1}$ K^{-2} are well documented to be mixed valence compounds. Shown in Fig. 2 are C/T vs. T^2 data for YbXCu$_4$ compounds with X=Ag, Au and Pd [13]. The rapid increase in C/T with decreasing T at the lower temperatures for the compounds with X=Au and Pd is associated with magnetic order, presumably antiferromagnetic in character, that occurs at the respective temperatures of approximately 0.8 and 0.6 K where there are peaks in the $C(T)$ data. The absence of an anomaly in $C(T)$ for YbAgCu$_4$ indicates that this compound does not exhibit magnetic order, at least down to 0.45 K. The values of γ estimated from linear extrapolation of the C/T vs. T^2 data to 0 K for the specimens with X=Ag and Pd are $\gamma(0) = 245 \pm 6$ and 200 mJ (mol Yb)$^{-1}$ K^{-2} respectively; for the compound with X=Au no reliable method of extrapolating the C/T vs. T^2 data to 0 K to obtain an estimate of $\gamma(0)$ was evident. Shown in Fig. 3 are $\chi(T)$ data for YbAgCu$_4$, which follow a
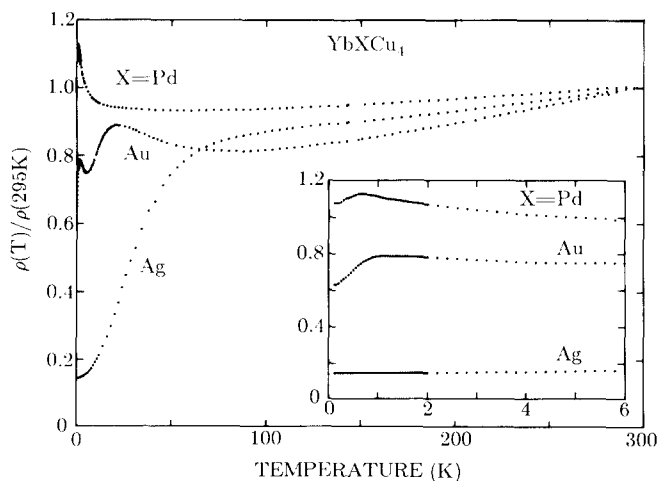

Fig. 1. Normalized electrical resistivity $\rho(T)/\rho(295\ \text{K})$ vs. temperature T for YbXCu$_4$ compounds with X=Ag, Au and Pd. Shown in the inset are the curves below 6 K. (From ref. 13.)

TABLE 1

Magnetic properties of ytterbium intermetallics-crystal structure, electronic specific heat coefficient γ, temperature T_{max} of the maximum in the magnetic susceptibility $\chi(T)$, effective magnetic moment μ_{eff}, Curie–Weiss temperature θ_p, Néel temperature T_N and extrapolated zero-temperature magnetic susceptibility $\chi(0)$ of various ytterbium compounds

Compound	Structure	γ (mJ (mol Yb)$^{-1}$ K^{-2})	T_{max} (K)	μ_{eff} (μ_B)	θ_p (K)	T_N (K)	$\chi(0) \times 10^3$ (cm^3 (mol Yb)$^{-1}$)	Ref.
YbAl$_2$	MgCu$_2$	16.8	850			n	0.52	33
YbIr$_2$	MgCu$_2$			4.49	−4	0.4		38
YbAl$_3$	Cu$_3$Au	45	125	4.2	−225	n	5.8	33
YbAu$_2$				4.5	−5			33
YbAu$_3$				4.5	−10	3		33, 34
YbAu$_4$				4.5	−10			33
YbCu$_{3.5}$		350		4.3	−68	n	32	19
YbCu$_{4.5}$		700		3.9	−25	n	46	19, 20
YbAlB$_4$	YCrB$_4$	125		3.8 ($\parallel c$)	−100 ($\parallel c$)	n	~20	35
YbAgCu$_4$	AuBe$_5$	245	35	4.28	−31	n	19.6	13
YbAuCu$_4$	AuBe$_5$	(200)		4.39	−8.8	0.6	275	13
YbPdCu$_4$	AuBe$_5$	200		4.33	−13.5	0.8	174	13
YbInCu$_4$	AuBe$_5$				(~70 K, valence transition)			36
YbB$_{12}$	UB$_{12}$				Hybridization gap			28
YbBe$_{13}$	NaZn$_{13}$					1.28		37
YbCuAl	Fe$_2$P	260	28	4.35	−34		13.6, 25.0	39
YbNiGa	Fe$_2$P			4.5	0			40
YbNi				4.5	−15			40
YbPd	CsCl			4.3	−160	0.5, 1.9		40, 41
YbInAu$_2$			100				5.8	46
YbPt				4.0	0			40
YbPt$_2$		124, 171				5 (f.m.)		42
YbPt$_3$	Cu$_3$Au	50		4.4	−3, −7	0.18, 0.3		42
Yb$_3$Pt$_4$	Pu$_3$Pd$_4$	76		4.54	−3.5	2.25		42
Yb$_3$Pd$_4$	Pu$_3$Pd$_4$	153		4.38	−12	3		42
Yb$_3$Pt$_5$	Monoclinic	28		4.56	−3.8	0.95		42
YbNiSn	ϵ-TiNiSn			4.3	−43	5.5 (f.m.)		14
Yb$_4$As$_3$	Th$_3$P$_4$	200		Heterogeneous mixed valent				43
Yb$_4$Sb$_3$	Th$_3$P$_4$		230	Heterogeneous mixed valent				44
Yb$_4$Bi$_3$	Th$_3$P$_4$			Heterogeneous mixed valent				44
YbCu$_2$Si$_2$	ThCr$_2$Si$_2$	135		4.19	−90	n		45
YbNi$_2$Ge$_2$	ThCr$_2$Si$_2$		40				18.5	46
YbP	NaCl			4.85	−55	0.41		21, 47
YbAs	NaCl			4.75	−45	0.58		21, 47
YbSb	NaCl				−60	0.32		21, 47
YbN	NaCl			4.95	−116	0.79		21, 47
YbSi	CrB	~900		4.21	−40	1.6		48
YbBiPt	MgAgAs	8000		4.2	−1	0.4		23

Curie–Weiss law between room temperature and about 100 K and then pass through a maximum at about 35 K before reaching a constant value at low temperature [13]. This behavior of $\chi(T)$ is similar to that reported for YbCuAl
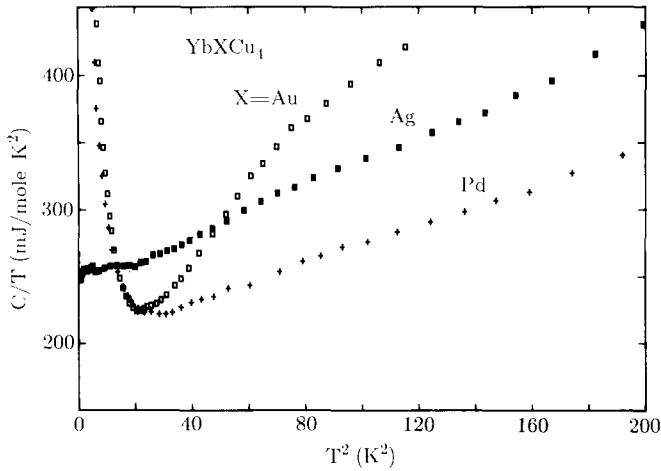
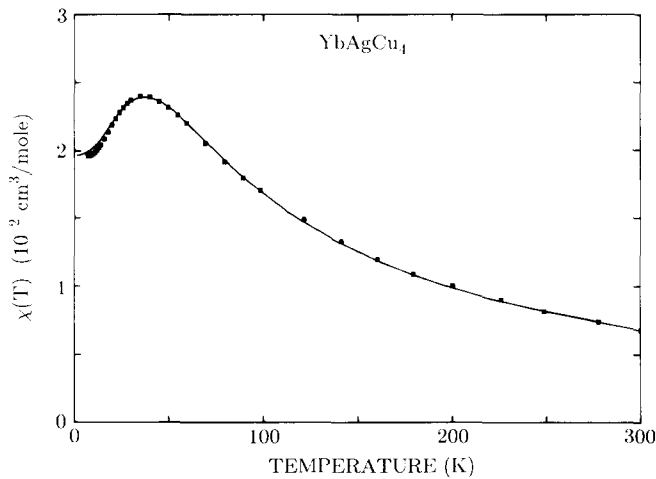Fig. 2. Specific heat C divided by temperature T vs. T^2 for YbXCu$_4$ compounds with X=Ag, Au and Pd. (From ref. 13.)

Fig. 3. Magnetic susceptibility χ vs. temperature T for YbAgCu$_4$. The solid curve is the calculated susceptibility $\chi(T)$ scaled to the zero-temperature value using the results of ref. 18 for the $J=\frac{7}{2}$ Coqblin–Schrieffer model. (From ref. 13.)

[17]. Rajan [18] has calculated $\chi(T)$ and the specific heat $C(T)$ in zero magnetic field for angular momentum values from $J=\frac{1}{2}$ to $\frac{7}{2}$ by solving the exact thermodynamic equations of the Coqblin–Schrieffer impurity model with the Bethe *ansatz*. As shown in Fig. 3, the numerical results of this model for $J=\frac{7}{2}$, the Yb^{3+} Hund's rules value (solid curve in the figure), provide an excellent description of the $\chi(T)$ data for YbAgCu$_4$. The value

of the characteristic temperature T_0 corresponding to this fit, $T_0 = 168$ K, yields a value for $\gamma(0)$ of 182 mJ mol^{-1} K^{-2}, which is in reasonable agreement with the experimental value of about 245 mJ mol^{-1} K^{-2}.

The range $100 \lesssim \gamma \lesssim 300$ mJ (mol Yb)$^{-1}$ K^{-2} is one where many compounds are found, most of which order magnetically, often with an integrated entropy to the magnetic ordering temperature less than $R\ln 2$ (mol Yb)$^{-1}$ (see Table 1). This range of γ is also one where a large number of cerium compounds are found. Larger γ materials are much less common for both cerium and ytterbium. A part of the reason for this is probably because large γ requires low T_K, and a simple argument suggests that magnetic interaction temperatures tend to be greater than T_K when T_K is small. This is to say that magnetic order curtails the development of a high γ ground state in this case. For cerium compounds we find a number of examples with $\gamma \gtrsim 1$ J (mol Ce)$^{-1}$ K^{-2}. It is in this last region that the comparison with ytterbium compounds presents some new features.

Two ytterbium materials with $\gamma \gtrsim 300$ mJ (mol Yb)$^{-1}$ K^{-2} have the formula YbCu$_x$, with $x = 3.5$ and 4.5 [19, 20]. The $x = 4.5$ material has one of the largest values of γ reported for an ytterbium material, 700 mJ (mol Yb)$^{-1}$ K^{-2}. In fact, it appears that this last material is disordered; the electrical resistivity continues to rise at low temperature, showing no sign of the formation of a coherent state. There is incomplete knowledge about the crystallography of this material and it is possible that the structure has stacking irregularities. We argue that this is a concentrated impurity system, not an atomically ordered heavy fermion material.

However, there is another very peculiar class of ytterbium materials which appears to have very low carrier concentration yet large γ. This class includes the ytterbium monopnictides [21], compounds such as Yb$_4$As$_3$ and analogues [22] and the half-Heusler compound YbBiPt [23]. This last compound has a specific heat with linear slope below 200 mK of 8 J (mol Yb)$^{-1}$ K^{-2}, which, if it is a legitimate γ, may make it the largest ever reported for an atomically ordered compound. While it would be surprising if such low carrier concentration materials develop a heavy fermion state, we really do not know enough to say that it cannot happen. In fact, the magnetic field dependence of both the specific heat and electrical resistivity is large and consistent with Kondo-like interactions underlying these properties. What seems odd here, of course, is the apparent semimetallic background. For the YbBiPt case we mention that LuBiPt has $\gamma \lesssim 1$ mJ (mol Yb)$^{-1}$ K^{-2} [23] and its isoelectronic partner YBiPt [23] has an electrical resistivity characteristic of a small gap semiconductor. We are not aware of cerium compounds analogous to YbBiPt.

It may be, however, that the physics of these particular ytterbium pnictides is related to that of the interesting small gap semiconductors known as hybridization gap materials. These materials include SmB$_6$ [24], the "gold" phase of SmS [24], CeFe$_4$P$_{12}$ [25], CeNiSn [26], Ce$_3$Bi$_4$Pt$_3$ [27], YbB$_{12}$ [28] and, perhaps, CeRhSn [29] and UFe$_4$P$_{12}$ [25]. The physics of these "hybridization gap" compounds appears to result from an "effective" f level

crossing and hybridizing with a conduction band at the Fermi level, and opening a gap there. The electron count must be such as to fill the lower hybridized band, and the gap, it can be argued, will be of the order of the Kondo temperature of the f element in the material without the gap. Perturbing such a hybridization gap material via added conduction electrons (by atomic substitution) is known to generate large γ per added impurity. We speculate that the group of ytterbium pnictides mentioned above may be related to the small T_K limit of the hybridization gap materials, but in a situation such that the hybridization is unable to gap the entire Fermi surface. In this viewpoint we arrive at some idea of where to search for the cerium analogues to the peculiar ytterbium materials.

There is one cerium heavy fermion superconductor known, $CeCu_2Si_2$, the material that was responsible for much of the initial interest in the field [30]. There are no superconductors formed by ytterbium except in the oxides [31] and the cleanly divalent ytterbium intermetallics such as the stannides [32]. We can hope to discover one day such an ytterbium heavy fermion superconductor, but the database from cerium compounds suggests that there will not be many of them.

4. Concluding remarks

There are a number of factors which make studying the physics of ytterbium materials particularly attractive. The first is that pressure tends to push the f^{13} level towards greater localization, exactly the opposite of the case with cerium. This drives $T_K \rightarrow 0$ K and has the effect of increasing γ. Ytterbium is, furthermore, a suitable nuclear magnetic resonance nucleus, unlike cerium. This gives us a probe exactly at the site of interest in heavy fermion materials. Ytterbium is additionally a Mössbauer nucleus, albeit not an especially good one, but again providing a probe at the center of interest. It is to be emphasized that such probes are important because the dominant interactions take place in the first coordination sphere surrounding the f atom.

A disadvantage of working with ytterbium materials comes from preparation difficulties associated with the high vapor pressure of ytterbium at temperatures needed to synthesize many compounds. However, there are ways around this, and in particular, wider experience with molten metallic flux techniques makes the investigation of ytterbium materials a particularly attractive field. We find good reason to believe that the f hole analogue of cerium shares the same f electron physics and that there are significant advantages to studying ytterbium systems in much greater detail.

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