Six closely related $\text{YbT}_2\text{Zn}_{20}$ ($T = \text{Fe, Co, Ru, Rh, Os, Ir}$) heavy fermion compounds with large local moment degeneracy

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Heavy fermion compounds represent one of the most strongly correlated forms of electronic matter and give rise to low temperature states that range from small moment ordering to exotic superconductivity, both of which are often in close proximity to quantum critical points. These strong electronic correlations are associated with the transfer of entropy from the local moment degrees of freedom to the conduction electrons, and, as such, are intimately related to the low temperature degeneracy of the (originally) moment bearing ion. Here we report the discovery of six closely related Yb-based heavy fermion compounds, $\text{YbT}_2\text{Zn}_{20}$, that are members of the larger family of dilute rare earth bearing compounds: $\text{RT}_2\text{Zn}_{20}$ ($T = \text{Fe, Co, Ru, Rh, Os, Ir}$). This discovery doubles the total number of Yb-based heavy fermion materials. Given these compounds' dilute nature, systematic changes in T only weakly perturb the Yb site and allow for insight into the effects of degeneracy on the thermodynamic and transport properties of these model correlated electron systems.

correlated electron | intermetallic compound

Heavy fermion compounds have been recognized as one of the premier examples of strongly correlated electron behavior for several decades. Ce- and U-based heavy fermion compounds have been well studied, and in recent years a small number of Yb-based heavy fermions have been identified as well (1–3). Unfortunately, in part due to the somewhat unpredictable nature of $4f$ ion hybridization with the conduction electrons, it has been difficult to find closely related (e.g., structurally) heavy fermion compounds, other than of the ThCr_2Si_2 structure, especially Yb-based ones, that allow for systematic studies of the Yb ion degeneracy. Part of this difficulty is associated with the fact that the $4f$ hybridization depends so strongly on the local environment of the rare earth ion.

Dilute, rare earth (R) bearing, intermetallic compounds are ordered materials with <5 atomic percent rare earth fully occupying a unique crystallographic site. Such materials offer the possibility of investigating the interaction between conduction electrons and $4f$ electrons in fully ordered compounds for relatively low concentrations of rare earths. For the case of $R = \text{Yb}$ or Ce , these materials offer the possibility of preserving low temperature, coherent effects while more closely approximating the single ion Kondo impurity limit. A very promising example of such compounds is derived from the family of $\text{RT}_2\text{Zn}_{20}$ (4) ($T =$ transition metal), which has recently been shown to allow for the tuning of the nonmagnetic $R = \text{Y}$ and Lu members to exceedingly close to the Stoner limit as well as allowing for the study of the effects of such a highly polarizable background on local moment magnetic ordering for $R = \text{Gd}$ (5).

Discovery

Here, we present thermodynamic and transport data on six strongly correlated Yb-based intermetallic compounds found in

the $\text{RT}_2\text{Zn}_{20}$ family for $T = \text{Fe, Co, Ru, Rh, Os, Ir}$, effectively doubling the number of known Yb-based heavy fermions (compounds with linear coefficient of specific heat, γ , >400 mJ/mol K^2 ; ref. 1). The $\text{RT}_2\text{Zn}_{20}$ compounds crystallize in the cubic $\text{CeCr}_2\text{Al}_{20}$ ($Fd\bar{3}m$ space group) structure (6, 7). Due to the relatively low concentration of rare earth, as well as transition metal, in these compounds, the four nearest neighbors as well as the 12 next-nearest neighbors of the rare earth ion are Zn atoms. The rare earth ion is coordinated by a 16-atom Frank–Kasper polyhedron and has a cubic point symmetry. This near spherical distribution of neighboring Zn atoms gives rise to the possibility of relatively low crystal-electric-field (CEF) split levels and also promises a large degree of similarity between this isostructural group of Yb-based heavy fermions. These compounds, then, not only greatly expand the number of known Yb-based heavy fermions, but, as will be shown below, also provide a route to studying how the degeneracy of the Yb ion at Kondo temperature, T_K , effects the low temperature-correlated state.

Thermodynamic and transport data taken on the six $\text{YbT}_2\text{Zn}_{20}$ compounds are presented in Figs. 1–3 and are summarized in Table 1. Whereas the temperature-dependent magnetic susceptibility, electrical resistivity, and specific heat for $T = \text{Fe, Ru, Rh, Os, Ir}$ are qualitatively similar, $\text{YbCo}_2\text{Zn}_{20}$ is, at first glance, somewhat different. Most conspicuously, instead of manifesting a clear loss of local moment behavior at low temperature (8), the temperature-dependent susceptibility continues to be Curie–Weiss-like down to 2 K (Fig. 1a *Inset*).

Focusing initially on the five, apparently similar, $\text{YbT}_2\text{Zn}_{20}$ compounds ($T = \text{Fe, Ru, Rh, Os, Ir}$), Fig. 1a and b demonstrates that each of these compounds appears to be an excellent example of a Yb-based heavy fermion with electronic specific heat, γ , values ranging between 500 and 800 mJ/mole K^2 . [The modest rise in the $\Delta C(T)/T$ data below 2 K is most probably associated with a nuclear Schottky anomaly and, for this work, is simply ignored. This assumption is further supported by the data and analysis presented in Fig. 5 below.] The low temperature magnetic susceptibility correlates well with the electronic specific heat values leading to the Wilson ratio (1, 2) for these five compounds having values of 1.1 and 1.3 (see Table 1). The temperature-dependent electrical resistivity data (Fig. 2) for these five compounds are also remarkably similar at high temperature and manifest clear T^2 temperature dependencies at low temperatures (see *Inset*). Although resistivity data were taken down to 20 mK, no indications of either magnetic order

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Fig. 1. Low temperature thermodynamic properties of $\text{YbT}_2\text{Zn}_{20}$ compounds ($T = \text{Fe, Ru, Rh, Os, Ir}$). (a) Magnetic susceptibility ($H = 0.1 \text{ T}$). (Inset) Temperature-dependent inverse susceptibility for $\text{YbCo}_2\text{Zn}_{20}$ and $\text{YbOs}_2\text{Zn}_{20}$. (b) Low temperature-specific heat, C , divided by temperature, as a function of T^2 .

or superconductivity were found for any of the $\text{YbT}_2\text{Zn}_{20}$ compounds.

The thermodynamic and transport properties of $\text{YbCo}_2\text{Zn}_{20}$ are somewhat different from the other five compounds. $\text{YbCo}_2\text{Zn}_{20}$ does not manifest the clear loss of local moment behavior, >1.8 K, in the susceptibility data (see Fig. 1*a Inset*) and the electrical resistivity and the specific heat only manifest Fermi-liquid-like behavior for $T \leq 0.2$ K (Fig. 3). Although the higher temperature electrical resistivity of $\text{YbCo}_2\text{Zn}_{20}$ is similar

Fig. 2. Temperature-dependent electrical resistivity of YbT₂Zn₂₀ compounds (T = Fe, Co, Ru, Rh, Os, Ir). (*Inset*) Low temperature electrical resistivity as a function of T^2 for T = Fe, Ru, Rh, Os, Ir; note separate axes for T = Os on top and right.

to the other five $\text{YbT}_2\text{Zn}_{20}$ compounds, it manifests a much clearer example of a resistance minimum and lower temperature coherence peak.

Analysis

Some of the salient parameters extracted from these data are summarized in Table 1 and the coefficient of the T^2 resistivity (A) is plotted as a function of the linear coefficient of the specific heat (γ) in a Kadowaki–Woods (KW) (8–10) type plot (Fig. 4). Perhaps the most noteworthy point that becomes clear from this presentation of the data is that, whereas there is relatively little variation in the low temperature thermodynamic properties, or Wilson ratio, associated with the $T = \text{Fe, Ru, Rh, Os, Ir}$ compounds, there is an order of magnitude variation in the value of the coefficient of the T^2 resistivity, A . This gives rise to a vertical spread of the KW data points.

Recent theoretical work (11, 19, 20) has generalized the idea of a fixed KW ratio to one that can vary by over an order of magnitude, depending upon the value of the degeneracy of the Yb ion when it hybridizes. Fig. 4 shows, as solid lines, the four degeneracies possible for the Kramers, Yb^{3+} ion. The $\text{YbT}_2\text{Zn}_{20}$ data indicate that for $T = \text{Fe, Ru}$ the Yb ion has a significantly larger degeneracy upon entering the Kondo-screened state than it does for the $T = \text{Rh, Os, Ir}$ compounds. The data point for

Table 1. Summary of structural, thermodynamic, and transport data on $\text{YbT}_2\text{Zn}_{20}$ compounds (T = Fe, Co, Ru, Rh, Os, Ir)

T	a , Å	Θ , K	μ_{eff} , μ_B	χ_0 , 10^{-3} cm^3 mole	χ_{max} , 10^{-3} cm^3 mole	$T_{\chi_{max}}$, K	ρ_0 , $\mu\Omega \text{ cm}$	A , $\frac{\mu\Omega \text{ cm}}{\text{K}^2}$	RRR	γ , mJ mol K^2	WR	KWR, $\frac{\mu\Omega \text{ cm mole}^2 \text{ K}^2}{\text{mJ}^2}$	N	T_K , K
Fe	14.062	−22.6	4.5	58.0	65.1	14.0	2.1	5.4×10^{-2} ($T \leq 11$ K)	31.2	520	1.2	2.0×10^{-7}	8	33
Co	14.005	−4.3	4.3	415.1			21	165 ($T \leq 0.2$ K)	2.8	7,900		27×10^{-7}	4	1.5
Ru	14.193	−15.5	4.5	58.9	65.4	13.5	5.3	6.8×10^{-2} ($T \leq 11$ K)	10.9	580	1.1	2.0×10^{-7}	8	30
Rh	14.150	−15.9	4.4	77.7	82.4	5.3	5.6	54×10^{-2} ($T \leq 6$ K)	11.8	740	1.3	10.1×10^{-7}	4	16
Os	14.205	−19.18	4.5	60.0	60.7	11.5	17	53×10^{-2} ($T \leq 1$ K)	4.4	580	1.1	15×10^{-7}	4	20
Ir	14.165	−23.8	4.4	55.9	56.3	6.5	8.8	33×10^{-2} ($T \leq 5$ K)	8.9	540	1.2	11×10^{-7}	4	21

Shown are cubic lattice parameter, a ; paramagnetic Curie–Weiss temperature, Θ , and effective moment, μ_{eff} , obtained from fit to inverse susceptibility between ≈ 100 and 300 K (after subtraction data from the nonmagnetic analogues, $\text{LuT}_2\text{Zn}_{20}$); low temperature magnetic susceptibility, χ_0 taken at 1.8 K; magnetic susceptibility at the maximum, χ_{max} and corresponding temperature, $T_{\chi max}$; residual resistivity, ρ_0 , taken at $T \approx 20$ mK; coefficient of the T^2 resistivity, A (with range of fit given below); residual resistivity ratio, RRR; linear coefficient of the specific heat, γ ; Wilson ratio, WR; Kadowaki–Woods ratio, KWR; degeneracy, N ; and estimated Kondo temperature, T_K .

Fig. 3. Low temperature electrical resistivity and C/T of $\text{YbCo}_2\text{Zn}_{20}$ as a function of T^2 .

$\text{YbCo}_2\text{Zn}_{20}$ approaches the far extreme of the KW plot, being near to the point associated with the exceptionally heavy fermion, YbBiPt (12, 13).

As mentioned above, the sole Yb site is one of cubic point symmetry and is surrounded only by Zn in a shell of very high coordination number. Based on these facts, it is anticipated that the Yb ion's Hund's rule, ground state multiplet will split into a quartet and two doublet states with a small total splitting. If, indeed, the difference between $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbRu}_2\text{Zn}_{20}$ on one hand and $\text{YbRh}_2\text{Zn}_{20}$, $\text{YbOs}_2\text{Zn}_{20}$ and $\text{YbIr}_2\text{Zn}_{20}$ on the other is the degree to which the Hund's rule ground state degeneracy has been lifted by crystalline electric field splitting before the Kondo screening takes place, then there should be some indication of this in other data as well. If, as Tsujii *et al.* suggest (11), the ratio of T_K to T_{CEF} is of primary concern, then an examination of Fig. 1a in the light of the Coqblin-Schrieffer model (refs. 8 and 21, specifically figure 1 of ref. 8) indicates that the larger the ratio of the maximum susceptibility to the low temperature susceptibility, the larger is the degeneracy that remains in the Yb system at T_K . The ratios of the maximum susceptibility to the low temperature susceptibility for $T = \text{Fe}$ and Ru are 1.12 and 1.11, respectively, whereas the ratios for $T = \text{Rh}$, Os , and Ir are 1.06, 1.01, and 1.01, respectively. These values are consistent with a difference in degeneracy of at least $\Delta N = 2$ (see Fig. 4).

This analysis can be made even more thoroughly by performing a fit (8) to the magnetic component of the specific heat over a wide temperature range. This is shown in Fig. 5a for $\text{YbFe}_2\text{Zn}_{20}$, the compound with the largest degeneracy inferred

Fig. 4. Log-log plot of A versus γ (Kadowaki-Woods plot) of six new $\text{YbT}_2\text{Zn}_{20}$ heavy fermion compounds ($T = \text{Fe}, \text{Co}, \text{Ru}, \text{Rh}, \text{Os}, \text{Ir}$) shown with representative data from ref. 11 as well as data for YbBiPt (12, 13), $\text{YbNi}_2\text{B}_2\text{C}$ (14), YbPtIn (15), YbAgGe (16), YbNiSi_3 (17), and YbIr_2Si_2 (18). The solid lines for degeneracies $N = 2, 4, 6$, and 8 are taken from ref. 11.

Fig. 5. Coqblin-Schrieffer analysis of magnetic specific heat data from $\text{YbFe}_2\text{Zn}_{20}$ (a) and $\text{YbRh}_2\text{Zn}_{20}$ (b) after subtraction data from the nonmagnetic analogues, $\text{LuFe}_2\text{Zn}_{20}$ and $\text{LuFe}_2\text{Rh}_{20}$, respectively. Data are shown as open symbols and best fits to $J = 1/2, 3/2, 5/2$, and $7/2$ using formalism described in ref. 8 are shown in black, red, green, and blue lines, respectively. T_K values from these fits are $\approx 37\text{ K}$ and $\approx 15\text{ K}$ for $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbRh}_2\text{Zn}_{20}$, respectively. For $\text{YbRh}_2\text{Zn}_{20}$, the Schottky contribution ($\Delta E_1 = 40\text{ K}$) is shown as a dashed red line; the sum of Schottky and Rajan ($J = 3/2$) terms is shown as a solid black line.

from the KW plot (Fig. 4) as well as from the above analysis. The data are best fit (and very well fit) by the $J = 7/2$ ($N = 8$) curve. These data are particularly compelling because the height of the anomaly is not an adjustable parameter once N is chosen. This analysis further confirms the degeneracy inferred from Fig. 4 and confirms that the low temperature, greatly enhanced, electronic specific heat is due to Kondo screening of the large N , Yb ion. Fig. 5a Inset shows the magnetic entropy as a function of temperature. By 60 K, it rises past the $J = 5/2$ value. The fact that it does not reach the $\text{Rln}8$ anticipated is most likely due to (i) difficulties in accurately modeling the nonmagnetic contribution with $\text{LuFe}_2\text{Zn}_{20}$ at high temperatures and (ii) difficulties associated with taking the difference between two large, comparable values, as well as the fact that by 60 K a recovery of the full $\text{Rln}8$ is not expected (see fit to $J = 7/2$ in Fig. 5a).

Fig. 5b presents similar data from $\text{YbRh}_2\text{Zn}_{20}$, one of the compounds that the KW analysis predicts to have a lower degeneracy. The maximum in the magnetic specific heat data falls between the $J = 3/2$ and $J = 5/2$ values, indicating that the CEF splitting scheme will not allow the very simple type of analysis on which refs. 8 and 21 are premised: i.e., one that has the CEF levels either at $T \ll T_K$ or $T \gg T_K$. These data can be well fit, though, by the addition of a Schottky anomaly associated with a $T \geq T_K$ CEF level. The low temperature part of the specific heat data can be well fit by assuming that a quadruplet is Kondo