



Magnetization, Maxwell's relations, and the local physics of $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$

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The dilute Kondo compound, $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$, displays non-Fermi-liquid behavior but no zero-point entropy; it thus appears to elude description by known single-ion models. It may also provide a clue to the underlying local degrees of freedom in its dense counterpart, URu_2Si_2 . Here we use high-resolution magnetization studies to cross-check the thermodynamic consistency of previous experiments. Measurement of the field dependence of the temperature scale, $T_F(H)$, associated with Fermi-liquid behavior probes the nature of the underlying impurity fixed point. We find that $T_F(H)$ grows linearly with applied field, in contrast to the quadratic form expected for the two-channel Kondo model. We use a scaling argument to show that the observed behavior of $T_F(H)$ is consistent with the absence of zero-point entropy, suggesting novel impurity behavior in this material. More generally, we suggest the field magnetization as a probe of single-ion physics and make predictions for its behavior in other actinide compounds.

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The non-Fermi-liquid physics of the dilute Kondo compound $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ (TURS) is an outstanding problem in heavy-fermion materials.^{1,2} The local degrees of freedom responsible for non-Fermi-liquid behavior in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ are widely believed to provide the Hilbert space for the hidden order in its dense counterpart, URu_2Si_2 ; thus understanding of the dense and the dilute systems may be closely linked. Furthermore, although TURS has been extensively studied experimentally,^{3,4} its unusual physics has eluded description by an established single-ion model known to display non-Fermi-liquid behavior. For example, a well-studied mechanism for non-Fermi-liquid behavior in an impurity system is provided by the two-channel Kondo model (TCKM), where competition between the channels results in quantum critical behavior accompanied by a fractional zero-point entropy.^{5,6} It has been proposed that this physics is realized in a number of heavy-fermion impurity systems characterized by quadrupolar or non-Kramers doublet ground states;⁷ $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ was initially thought to be an excellent candidate. In particular, experiments^{3,4} indicate $\gamma \equiv \frac{c_p}{T}$, $\chi \sim \ln T$ at low temperatures and application of a magnetic field (H) drives the system into a Fermi liquid with $\gamma, \chi \sim \log H$. However the two-channel Kondo model proposal fails in a crucial way since application of H quenches the fractional zero-point entropy, the two-channel Kondo model predicts a field-induced Schottky anomaly in the specific heat (c_p). However, in contrast to the situation⁸ in $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$, this is not observed^{3,4} in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ and so the fractional zero-point entropy predicted by the two-channel Kondo model⁹ appears to be absent. Here we return to this problem in TURS spurred by renewed interest in the dense system URu_2Si_2 . We show that high-resolution magnetization studies provide a cross-check on the thermodynamic consistency of previous specific-heat experiments. More specifically, measurements of the field dependence of the temperature scale, $T_F(H)$, associated with Fermi-liquid behavior probes the nature of the underlying impurity fixed point. We therefore study whether the failure to observe the fractional zero-point entropy in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ is an experi-

mental issue or whether it indicates the presence of a fundamentally new class of impurity behavior.

The magnetization, in conjunction with Maxwell's thermodynamic relations, can be used to cross-check specific-heat measurements. For a system with magnetic moment m , Maxwell's relation

$$\frac{\partial^2 F}{\partial H \partial T} = -\frac{\partial m}{\partial T} = -\frac{\partial S}{\partial H} \quad (1)$$

leads to

$$\Delta S = \int \int \frac{\partial \chi}{\partial T} dH' dH = \int \frac{\partial m}{\partial T} dH \quad (2)$$

so that

$$S(T, H) - S(T, 0) = \int_0^H \frac{\partial m(T, H')}{\partial T} dH'. \quad (3)$$

Taking the zero-temperature limit of this equation at finite H , we obtain

$$\lim_{T \rightarrow 0} [S(T, H) - S(T, 0)] = \lim_{T \rightarrow 0} \int_0^H \frac{\partial m(T, H')}{\partial T} dH'. \quad (4)$$

If there is zero-point entropy S_{ZP} in the non-Fermi-liquid state, then at zero field $\lim_{T \rightarrow 0} S(T, 0) = S_{ZP}$, however in a finite field $H > 0$, a Fermi liquid develops and $\lim_{T \rightarrow 0} S(T, H) = 0$. It follows that

$$-S_{ZP} = \lim_{T \rightarrow 0} \int_0^H \frac{\partial m(T, H')}{\partial T} dH'. \quad (5)$$

Since this expression holds for arbitrarily small magnetic fields H , it follows that if a zero-point entropy is present, the temperature derivative of the magnetization must sharpen up like a delta function as the temperature is reduced to zero [$\lim_{T \rightarrow 0} \frac{\partial m(T, H)}{\partial T} \sim -2S_{ZP} \delta(H)$]. Since high-resolution magnetization measurements do not have the subtraction issues associated with c_p experiments, Eq. (5) can be used to cross-

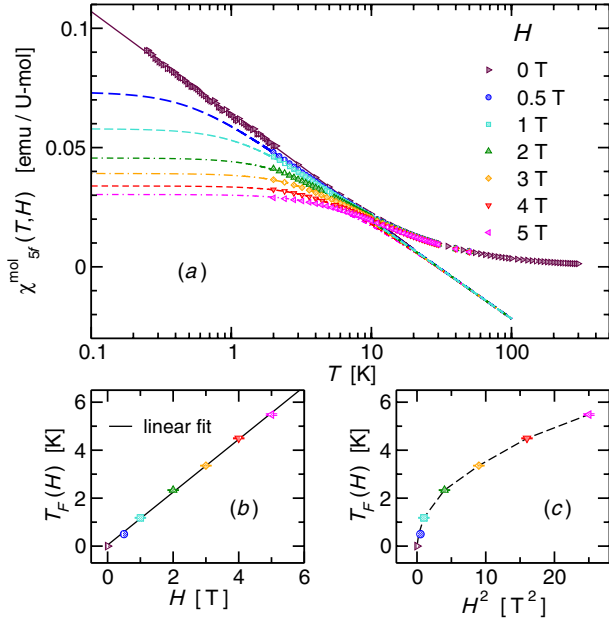


FIG. 1. (Color online) (a) Molar susceptibility, χ_{5f}^{mol} of U in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ for $x=0.03$ as the function of temperature for applied fields ranging from $H=0-5$ T. Lines indicate the best fit to the data below 6 K with the form $\chi_0 \ln[T_K/\sqrt{T^2+T_F(H)^2}]$, with $\chi_0 = 0.018 \pm 10^{-3}$ emu/U mol and $T_K = 29.8 \pm 0.3$ K. The crossover scale, $T_F(H)$ is plotted on (b) linear and (c) quadratic scales. The uncertainty of the fit for the parameter $T_F(H=0 \text{ T})=0$ is much smaller than the symbol size, while the value, $T_F(H=0.5 \text{ T})=0.5$ K has been fixed.

check the zero-point entropy result for $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$.

Single-crystal samples of $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ ($x=0$ and $x=0.03$) were grown using the Czochralski technique in a tri-arc furnace under a high-purity argon atmosphere. Powder x-ray diffraction studies on the crushed crystals confirmed that the obtained crystals are single phase. Magnetization measurements in a high-temperature range between 2 and 300 K were performed using a commercial superconducting quantum interference device magnetometer (Quantum Design Co., Magnetic Property Measurement System) in an applied magnetic field of 5 kOe. In this temperature and field range the magnetization M , measured at constant temperature, is linearly proportional to the field H ; thus the susceptibility χ is simply evaluated as $\chi=M/H$. In the lower temperature range from 0.24 to 4 K, χ is measured directly using the standard Hartshorn-bridge ac method in an ac field of 8 Oe at 80 Hz. The electrical resistivity, with current along the a axis, was measured using a standard four-probe ac method.

In Fig. 1(a), we show the T dependence of χ_{5f}^{mol} , the molar susceptibility of U in TURS for $x=0.03$, in magnetic fields between $H=0$ and 5 T. Noting the logarithmic behavior in χ close to the quantum critical point at zero temperature and magnetic field, we can model it with the simple expression

$$\chi_{5f}^{mol}(T, H) = -\chi_0 \ln \frac{\sqrt{T^2 + T_F(H)^2}}{T_K}. \quad (6)$$

Fitting this form to the data below $T=6$ K, we obtain $\chi_0 = 0.018 \pm 10^{-3}$ emu/U mol, $T_K = 29.8 \pm 0.3$ K. Figures

1(b) and 1(c) show the field-dependent crossover temperature, $T_F(H)$ on linear and quadratic scales. Its markedly linear magnetic field dependence contrasts strikingly with the quadratic behavior characterizing the two-channel Kondo model. The crossover scale $k_B T_F(H)$ is quantitatively the magnitude of a Zeeman energy

$$k_B T_F(H) = (gS)\mu_B H \equiv k_B h \quad (7)$$

with a g factor of $gS=1.6$ where we have introduced the reduced field, $h \equiv (gS)\mu_B H/k_B$. The appearance of a Zeeman splitting in the temperature dependence of the magnetic susceptibility is an indication that the underlying single-ion ground state of TURS is a magnetic multiplet. The value $gS=1.6$ would correspond to a Ising magnetic moment $gS \times \mu_B = 1.6 \times \mu_B$ a value consistent with previous estimates for a magnetic Γ_5 doublet.³ In the hexadecapolar Kondo effect scenario,¹⁰ $g=3.2 \cos(\phi)$, which then sets the mixing angle to be $\phi = \frac{2\pi}{3}$ in the dilute limit.

Since the phenomenological fit Eq. (6) to the susceptibility data can be written as

$$\chi \propto -\ln[T^2 + T_F(H)^2] + cst, \quad (8)$$

$$\ln[T^2 + T_F(H)^2] \propto \text{Re} \ln[T_F(H) - iT], \quad (9)$$

this leads to

$$\frac{\partial \chi}{\partial T} \propto \text{Im} \frac{1}{T_F(H) - iT}. \quad (10)$$

Replacing $T_F(H)$ with h (assuming that h is linear in H) and using the Maxwell relation [Eq. (2)], we obtain a phenomenological form for the entropy

$$\Delta S(T, h) \propto \text{Im}[(h - iT)\ln(h - iT) + iT \ln(-iT) - h \log(-i)], \quad (11)$$

where $\Delta S(T, h) = S(T, h) - S(T, 0)$. $\Delta S(T, h)$ is a regular smooth function for the full phase region that includes $h > T$ and $T > h$. More explicitly

$$\lim_{H \rightarrow 0} \lim_{T \rightarrow 0} \Delta S(T, h) = \lim_{T \rightarrow 0} \lim_{H \rightarrow 0} \Delta S(T, h) = 0, \quad (12)$$

indicating that there is no order-of-limits issue, no irregularity and thus no zero-point entropy; this is consistent with the previous specific-heat results.^{3,4}

We can also understand this absence of zero-point entropy using a more general scaling argument where we assume a regular scaling function

$$\chi \sim h^{-\nu}, \quad (13)$$

where, from experiment, the case of $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ can be understood as the marginal limiting case where $\nu=0$. We can write a general scaling form for the free energy

$$F \sim h^{2-\nu} \Phi\left(\frac{T}{h^\eta}\right), \quad (14)$$

where η refers to the field dependence of the crossover scale, $T_F(H)$, and we assume that $\Phi(x)$ is a slowly varying function of x . Then

$$F \sim T^{2-\nu} \eta \Phi_1 \left(\frac{h}{T^{1/\eta}} \right) \quad (15)$$

and

$$S = - \frac{\partial F}{\partial T} = T^{2-\nu/\eta-1} \Phi_2 \left(\frac{h}{T^{1/\eta}} \right), \quad (16)$$

where we note that for the measured $\eta=1$ and $\nu=0+\epsilon$, we recover $\gamma \sim \ln T$ consistent with experiment, where we have assumed that $\Phi_2(0)$ is a constant.

In order to have a finite zero-point entropy, the exponent of the temperature in Eq. (15) must be zero; then we must have

$$\eta = 2 - \nu, \quad (17)$$

where the scaling function has the behavior $\Phi_2(0)$ is the zero-point entropy [and $\Phi_2(\infty)=0$]. We see that to have a finite zero-point entropy for $\nu=0$ (TURS case), $\eta=2$ is required as is realized in the two-channel Kondo model (spin $S=1/2$); thus the absence of an observed zero-point entropy is consistent with the measured $\eta=1$. More specifically, the fitting function, Eq. (8), does not satisfy Eq. (17), consistent with the above scaling treatment. As an aside, we note that this simple scaling argument cannot reproduce the $\gamma \sim \ln T$ associated with the two-channel Kondo model; this behavior arises an additional $T^2 \ln T$ term in the free energy driven by the scaling of the leading irrelevant operators, and thus is inaccessible from a leading-order scaling treatment.

The scaling relation [Eq. (17)] is realized in all over-screened Kondo models, where the number of screening channels k is greater than $2S$. There the exponents, η and ν , and the number of screening channels, k , are related by¹¹⁻¹⁴

$$\eta = 1 + \frac{2}{k}, \quad \nu = 1 - \frac{2}{k}. \quad (18)$$

Further support for the $\frac{H}{T}$ scaling comes from resistivity data shown in Fig. 2 again for a TURS sample with $x=0.03$. We have fit it with the form

$$\rho = \rho_0 \ln \left[\sqrt{T^2 + T_R(H)^2} / T_0 \right], \quad (19)$$

where $T_R(H)$ is the dynamical crossover scale for Fermi-liquid behavior to develop. Once again we see a linear H dependence of this crossover scale; because we only have at most two decades of data we do not present it as a scaling plot. The fact that $T_R(H)$ and $T_F(H)$ are proportional to each other but are not equal reflects that the H/T scaling functions associated with thermodynamics and transport are most likely different. More field-dependent measurements of thermodynamic responses and resistivity at low fields and temperatures on TURS would provide more specifics about the nature of these scaling functions.

It is intriguing that the zero-field properties of TURS significantly overlap with those of the TCKM but that application of a magnetic field yields two very different field-induced Fermi liquids: in the TCKM the Fermi temperature grows quadratically with field whereas in TURS it is linear in field, as illustrated in Fig. 3. The two-channel Kondo model has a residual zero-point entropy, yet TURS has none; more-

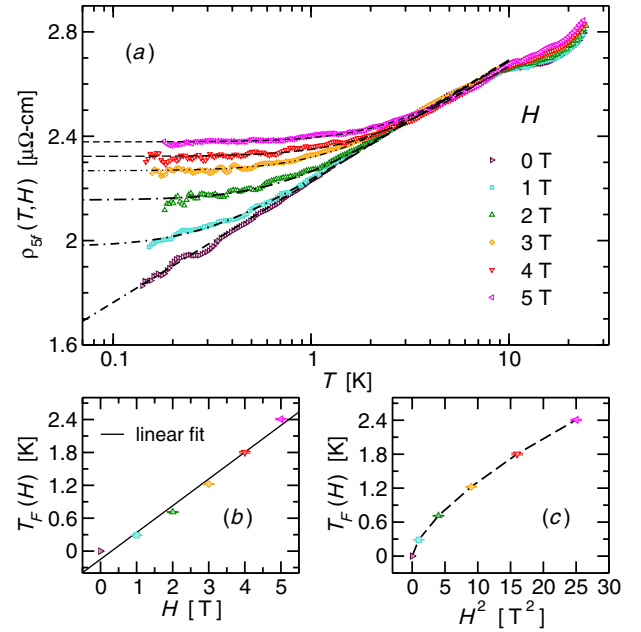


FIG. 2. (Color online) (a) Electrical resistivity for currents along the a axis in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ for $x=0.03$, $[\rho_{5f}(T, H)]$ as the function of T , for various fields between 0 and 5 T. Dashed lines indicate the best fits to the data below 9.5 K with the form $\rho_0 \ln[\sqrt{T^2 + T_R(H)^2}/T_0]$, with $\rho_0 = 0.201 \pm 0.002 \mu\Omega \text{ cm}$ and $T_0 = (1.6 \pm 0.1) \times 10^{-5} \text{ K}$. The crossover scale, $T_F(H)$ vs H and $T_F(H)$ vs H^2 , are shown on plots (b) and (c). There the standard errors coming from the nonlinear fit are smaller than the symbol size.

over these two features can be related by scaling arguments. Taken together these clear differences suggest a new kind of impurity fixed-point behavior with a novel kind of non-Fermi-liquid behavior. What kind of Kondo model can account for this distinct physics?

Kondo models involve small localized Hilbert spaces describing spin and orbital degrees of freedom coupled to one or more conduction baths. The generic ground state of an asymmetric Kondo model is a Fermi liquid. However, if the competing screening channels are symmetry equivalent, then non-Fermi-liquid behavior and a residual entropy result. Is there a deviation from perfect channel symmetry, that is, at once strong enough to destroy the zero-point entropy while remaining weak enough to preserve some type of non-Fermi-liquid behavior? In two-channel Kondo models, deviation from channel symmetry on the Fermi surface immediately leads to Fermi-liquid behavior. In principle, this leaves open the possibility of a *marginal* channel asymmetry that is ab-

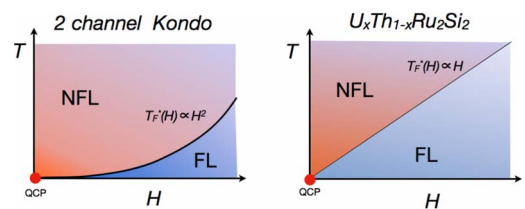


FIG. 3. (Color online) Schematic phase diagram for (a) two-channel Kondo model compared with experimentally determined phase diagram for (b) $\text{U}_x\text{Th}_{1-x}\text{Ru}_2\text{Si}_2$.

sent at the Fermi surface but grows as one moves away from it. For example, in the Γ_5 scenario,^{3,15} one isospin direction is odd under time reversal whereas the other two are even. Thus there is weaker symmetry protection than in the usual two-channel Kondo scenario,¹⁶ and further investigation is necessary to see whether marginal channel asymmetries exist here. We also note that an intermediate asymptotic regime with $T_F(H) \propto H$ can be obtained within the hexadecapolar Kondo scenario provided that the crystal-field splitting between the Γ_1 and the Γ_2 singlets is smaller than the Kondo temperature.¹⁷

In conclusion, we have used high-resolution magnetization measurements to confirm the absence of a zero-point entropy in TURS. Exploiting the fact that an applied field restores Fermi-liquid behavior in TURS, we find that the field-dependent Fermi temperature $T_F(H)$ scales *linearly* with field rather than the quadratic behavior expected for the

two-channel Kondo model. Since this technique does not depend on subtraction issues, it would be interesting to apply it to various impurity systems previously found to display quadrupolar Kondo behavior⁸ where we expect $T_F(H) \sim H^4$ or $T_F(s) \sim s^2$, where s is strain. Of particular interest is the quadrupolar Kondo candidate¹⁸ $\text{Pr}_x\text{La}_{1-x}\text{Pb}_3$ for $x \leq 0.05$ where no zero-point entropy has been observed. Finally, we would like to encourage more low-field and low-temperature measurements on $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ to learn more about the nature of its underlying impurity fixed point.

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