Quantum Critical $5f$ Electrons Avoid Singularities in $U(Ru, Rh)_2Si_2$

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We present specific heat measurements of 4% Rh-doped URu_2Si_2 at magnetic fields around the proposed metamagnetic transition field $H_m \sim 34$ T, revealing striking similarities to the isotructural Ce analog $CeRu_2Si_2$ for $H > H_m$. This suggests that strongly renormalized hybridized-band models apply equally well to both systems. The vanishing bandwidths as $H \rightarrow H_m$ are consistent with a quantum-critical point close to H_m. The existence of a phase transition into an ordered phase in the vicinity of H_m for 4% Rh-doped URu_2Si_2, but not for $CeRu_2Si_2$, is consistent with a stronger superexchange in the case of the U $5f$ system. Irreversible processes at the transition indicate a strong coupling of the $5f$ orbitals to the lattice, most suggestive of electric quadrupolar order.

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A quantum-critical point is a singular feature in the phase diagram of matter at the absolute zero of temperature [1,2]. At this point, the quantum fluctuations that result from the Heisenberg uncertainty principle acquire a divergent characteristic length [1,2]. Quantum fluctuations originating from this singularity influence the physical properties of matter over an expanding region of phase space (pressure, magnetic field, and chemical doping) as the temperature increases [3]. Several unexpected ordered states in strongly correlated matter, including unconventional superconductivity in f-electron intermetallics [4] and d-electron oxides [5,6], occur in the vicinity of a magnetic quantum-critical point. Consequently, theoretical models have focused on the role of symmetry-breaking quantum-critical points in their formation [3–5].

In this Letter, we present the first direct thermodynamic evidence for the avoidance of a nonsymmetry-breaking quantum-critical point by the creation of a new low temperature ordered state. In this case, quantum criticality is caused by metamagnetism induced by strong magnetic fields in 4% Rh-doped URu_2Si_2 [7], where Rh substitutes Ru so as to yield $URu_{1.92}Rh_{0.08}Si_2$. The 4%-doped sample has an advantage over pure URu_2Si_2 in that the hidden order phase is suppressed with a minimal amount of doping, leading to a much simpler phase diagram with only a single field-induced phase (phase II), while the metamagnetism remains mostly unchanged [7]. Our specific heat measurements reveal the presence of narrow $5f$ bands at high magnetic fields, whose entropy then drops abruptly on entry in this ordered phase at a distinct first-order phase transition. Irreversibility of the transition yields that it is of first order, suggestive of a strong coupling of the ordering $5f$-electron degrees of freedom to the lattice.

URu_2Si_2 [8] and its Rh-doped alloys [9] belong to a class of strongly-correlated metals [10] that includes $CeRu_2Si_2$ [11], UPt_3 [12], and $Sr_3Ru_2O_7$ [13], in which the d or f electrons are itinerant (i.e., they contribute to the metallic properties of the material) but are on the threshold of becoming localized and giving rise to magnetism. By coupling directly to their spin degrees of freedom, strong magnetic fields can coax the d or f electrons into a polarized state. ''Metamagnetism'' results when this transformation occurs abruptly at a critical magnetic field H_m, as depicted in Fig. 1(a). Should H_m evolve from a crossover at finite temperatures into a phase transition (analogous to that of a liquid-gas phase transition) very close to absolute zero [14], it then develops all of the characteristics of an isolated nonsymmetry-breaking quantum-critical point [15], as depicted in Fig. 1(b). Stoichiometric URu_2Si_2, $CeRu_2Si_2$, and $Sr_3Ru_2O_7$ [13] are sufficiently close to quantum criticality at H_m for their physical properties to be strongly influenced by fluctuations at temperatures $T \gtrsim 1$ K.

Being composed of $5f$ electrons that have properties intermediate between those of the d electrons in transition metal oxides and $4f$ electrons in rare earth intermetallics [16], actinide intermetallics such as $U(Ru, Rh)_2Si_2$ occupy a unique vantage point for understanding the dynamics of quantum criticality in the formation of new states. While not as spatially extended as d orbitals, the $5f$ orbitals of U exhibit a sizeable degree of superexchange between neighboring U sites [10], greatly increasing the likelihood of an ordered state over its $4f$ analogue, Ce. As with $4f$ electrons, however, the on-site Coulomb repulsion between $5f$ electrons is sufficiently strong to facilitate the formation of renormalized (narrow) bands upon their hybridization with regular conduction bands [17]. This has two immediate benefits: first, the narrow $5f$ band can be completely polarized by magnetic fields that are available in the laboratory. H_m in $URu_{1.92}Rh_{0.08}Si_2$ occurs at $\sim$34.4 T [7,18],

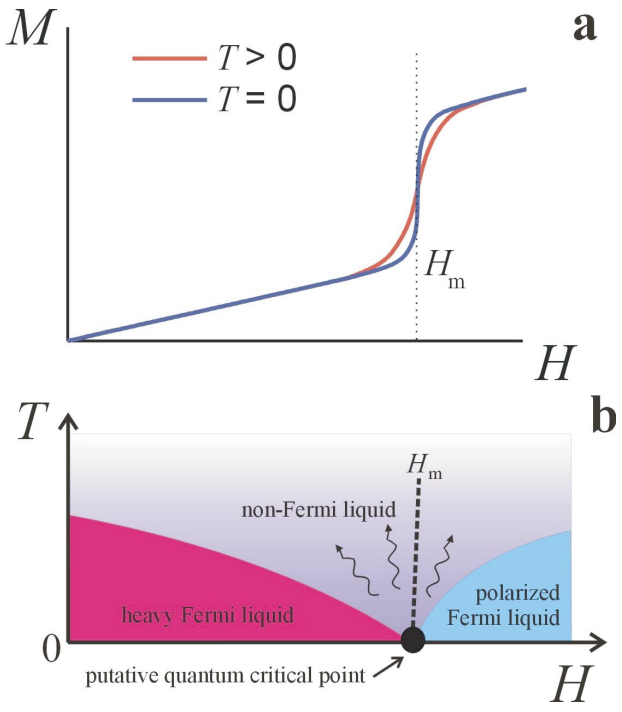

FIG. 1 (color). (a) An illustration of the inflection point in the magnetization at H_m, anticipated to acquire an infinite slope at $T = 0$ (blue line) but thermally broadened at finite temperatures $T > 0$ (red line). (b) The resultant magnetic field H versus temperature T phase diagram, with a heavy Fermi liquid region at $H < H_m$ and polarized Fermi liquid region at $H > H_m$. Only if quantum criticality is perfectly tuned is it a non-Fermi liquid at $T = 0$ and $H = H_m$ (black spot). At finite temperatures $T > 0$, the region of phase space occupied by the non-Fermi liquid expands (giving rise to the recognizable funnel shape), and in doing so, relieves the necessity for the quantum criticality being precisely tuned by pressure or chemical doping $T = 0$.

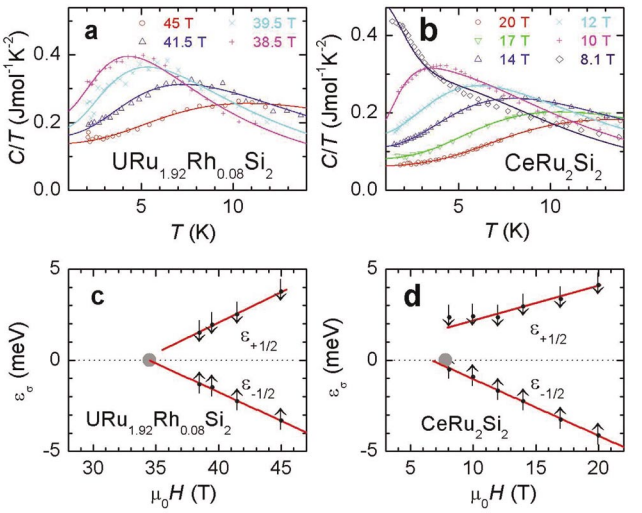

FIG. 2 (color). (a) Measured C_p/T $URu_{1.92}Rh_{0.08}Si_2$ vs temperature T at several different values of the magnetic field $H > H_m$, depicted using different symbols and colors as indicated. Solid lines indicate the fits to the hybridized-band model. (b) Published results for $CeRu_2Si_2$ together with fits to the hybridized-band model. (c) Fitted values for the position of the spin-up $\varepsilon_{-1/2}$ (up arrows) and spin-down $\varepsilon_{+1/2}$ (down arrows) hybridized bands in $URu_{1.92}Rh_{0.08}Si_2$, with red line linear fits added to guide the eye. A pseudospin notation of $\pm 1/2$ is used for down- and up-spin states, respectively. The gray dot represents the approximate location of the quantum-critical point or H_m [7,18]. (d) Similar fitted values for $CeRu_2Si_2$.

bringing it well within the limits (~ 45 T) of the highest available static magnetic fields. Second, the Fermi temperature ($T^* < 20$ K) of these quasiparticle bands is significantly lower than the characteristic Debye temperature ($T_\theta \gg 30$ K) of the phonons (or lattice vibrations) [19], making the magnetic field-dependent degrees of freedom of these polarized bands readily accessible to fundamental thermodynamic probes such as the specific heat [20]. By comparison, the comparatively large energy scale for d bands in the cuprates [5] continues to be a major impediment in attempts to identify a possible link between quantum criticality and phase formation in the high temperature superconductors.

Figure 2(a) shows the temperature dependence of the specific heat of $URu_{1.92}Rh_{0.08}Si_2$ divided by temperature C_p/T at several values of the magnetic field H. The relatively small contribution from the phonons for $T <$ 20 K (estimated from nonmagnetic $ThRu_2Si_2$) [19] implies that C_p/T in Fig. 2(a) is dominated by the electronic contribution, having an appearance similar to that of a Schottky anomaly, but with an additional quadratic tail at low temperatures. In order to understand this behavior for C_p/T, it is instructive to compare it with similar data obtained by van der Meulen *et al.* [21] for the isostructural Ce analog $CeRu_2Si_2$ (also a metamagnet) shown in Fig. 2(b), for which superexchange interactions between neighboring $4f$ sites are expected to be comparatively unimportant [10]. The overall electronic structure of $CeRu_2Si_2$ at fields $H > H_m$ has already been shown to be consistent with the general theoretical framework of the Anderson lattice model in which the $4f^1$ magnetic doublets are hybridized with a broad conduction band [22,23]. Following the qualitative picture of Edwards and Green [23] for the evolution of the quasiparticle up and down bands, we can approximate the corresponding density of electronic states (per unit of energy) by

$$D(\varepsilon) \approx D_0\left(1 + \Sigma_\sigma \frac{q_\sigma V^2}{(\varepsilon - \mu - \varepsilon_\sigma)^2 + \Delta^2}\right). \qquad (1)$$

D_0 is the density of states of the broad unperturbed conduction band, V is the hybridization potential, while ε_σ is the energy shift of each quasiparticle band due to the interplay between the Kondo interaction, and the Zeeman (or magnetic field) coupling at fields $H > H_m$. q_σ^{-1} represents the extent to which the density of electronic states is

renormalized by the strong Coulomb interactions between f electrons [23]. The parameter $\Delta = \pi q_\sigma V^2/D_0$ has to be adjusted to accommodate one electron per formula unit, becoming the effective width of the hybridized bands [23]. Although the important spectral weight around the bare f level is missing in this approach, it is entirely adequate for calculating C_v of $CeRu_2Si_2$ in the limit $|\varepsilon_\sigma - \mu| > \Delta$. Hence, Eq. (1) develops a simple Lorentzian form.

Figures 2(c) and 2(d) illustrate the results of fits for C_p/T versus T [shown as solid lines in Figs. 2(a) and 2(b)] where $C_p \sim C_v = T\partial^2 F/\partial T^2|_v$ is calculated numerically from the free energy $F = \int_{-\infty}^{\infty} D(\varepsilon) \ln[1 + \exp(\mu - \varepsilon)/k_B T] d\varepsilon$ [24] and where each spin component $\sigma = \pm 1/2$ is considered independent in the present hybridized-band approximation. These fits are in accordance with theoretical expectations for the Anderson lattice [22,23].

The close similarity of Figs. 2(a) and 2(b) and Figs. 2(c) and 2(d) implies that there exists an extensive range of magnetic fields and temperatures for which the hybridized-band model applies equally well to the $5f$ electrons in $URu_{1.92}Rh_{0.08}Si_2$ as it does to the $4f$ electrons in $CeRu_2Si_2$. It also implies that the orbital manifold of U in $U(Ru, Rh)_2Si_2$ is a doublet, as opposed to a singlet, which has been one of the pivotal areas of debate in attempts to understand the hidden order phase in pure URu_2Si_2 (suppressed in Rh-doped URu_2Si_2) [8–10,25–27]. Figure 3 further shows that the fitted bandwidth Δ for both $URu_{1.92}Rh_{0.08}Si_2$ and $CeRu_2Si_2$ plotted versus $H - H_m$, is the same for both systems, within experimental uncertainty. For both systems, $\Delta \propto q_\sigma$, revealing that the bands become progressively more narrow as the spin fluctuations intensify, since $q_\sigma^{-1} \propto |H - H_m|^{-1}$ exhibits a divergent behavior near H_m. The dashed line in Fig. 3 shows an independent estimate of the Fermi temperature T^* of the quasiparticle bands obtained from magnetotransport measurements on $URu_{1.92}Rh_{0.08}Si_2$ [7]. Its consistency with Δ provides the first confirmation of a direct correlation between features observed in the electrical resistivity and the hybridized bandwidth [22,23].

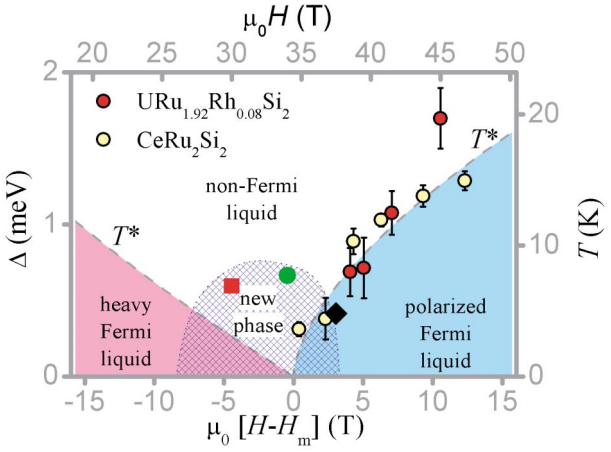

FIG. 3 (color). Fitted values of the hybridized bandwidth Δ for both $URu_{1.92}Rh_{0.08}Si_2$ and $CeRu_2Si_2$, as indicated, plotted vs $H - H_m$ (and also H in the former case). The dashed gray lines denote the regions of Fermi liquid and non-Fermi liquid recently identified from a crossover T^* in the electrical resistivity [7]. The vertical axes Δ and T are scaled only by the Boltzmann constant k_B, revealing that $k_B T^* \approx \Delta$. The various colored regions are labeled in accordance with Fig. 1, with the addition of a new phase (hashed region from Kim *et al.* [7]) which forms only in $URu_{1.92}Rh_{0.08}Si_2$ (not $CeRu_2Si_2$) as a means to avoid the putative quantum-critical point. The maxima in C_p vs T associated with this phase boundary are represented by colored symbols as presented in Fig. 4.

While $URu_{1.92}Rh_{0.08}Si_2$ and $CeRu_2Si_2$ possess many similarities for $H - H_m \gtrsim 4$ T, significant differences emerge as $H \rightarrow H_m$, as shown in Fig. 4. This can been seen rather directly in $URu_{1.92}Rh_{0.08}Si_2$ as soon as $\mu_0 H$ is reduced from 38 T to 37.5 T in Fig. 4(a). At temperatures above ~6 K, C_p/T at $\mu_0 H \sim 37.5$ T conforms to the solid curve calculated using fitting results for Δ, $\varepsilon_{+1/2}$, and $\varepsilon_{-1/2}$ extrapolated from $\mu_0 H \geq 38$ T in Fig. 2(c). Thus, at higher temperatures, the specific heat of $URu_{1.92}Rh_{0.08}Si_2$ at 37.5 T continues to be consistent with quasiparticle bands that become progressively more narrow and closer to μ as $H \rightarrow H_m$. At temperatures below 6 K, however, a significant redistribution of entropy occurs with respect to the calculated curve (cyan shaded area), establishing rather conclusively that the same $5f$ electrons involved in the formation of the quasiparticle bands condense into a new state at low temperatures.

The sharp anomaly at ~4.8 K at 37.5 K provides unambiguous evidence for the existence of a phase transition. Figure 4(b) further shows that the amount of energy required to heat the sample during the specific heat measure-

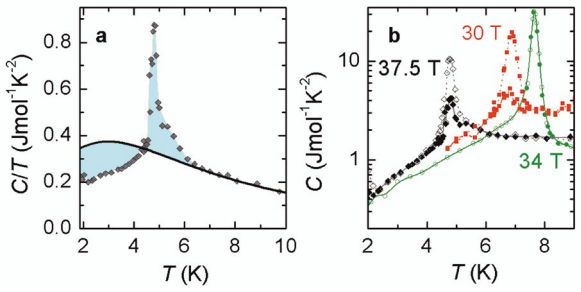

FIG. 4 (color). (a) Actual C_p/T data (diamonds) with a calculated curve (solid line) using parameters extrapolated to 37.5 T, obtained by fitting the hybridized-band model for $\mu_0 H \geq 38$ T. The calculated curve matches the data for $T > 6$ K, but the difference (shaded regions) reveals a significant redistribution of entropy below 6 K. (b) C_p vs T at several different magnetic fields (different colors) on both the initial ≈ 0.1 K increase of the temperature (open symbols) and subsequent increases of temperature after cooling (filled symbols), including the data presented in (a). The difference between open and filled plots provides definitive evidence for hysteretic losses.

ment at 28 and 37.5 T differs considerably between initial (open symbols) and subsequent (filled symbols) ≈ 0.1 K cycles of the temperature, using the relaxation method. Hence, the actual phase transformation itself is an energetically costly process, resulting in considerable hysteretic losses characteristic of a first-order phase transition [28]. This observation closely reproduces that observed at the first-order valence transition in $YbInCu_4$ [29,30], at which a change in the orbital manifold of the f electrons is coupled to the lattice parameters [31]. This finding in $URu_{1.92}Rh_{0.08}Si_2$ is most suggestive of orbital or electric quadrupolar order [27]. The absence of hysteresis at 34 T appears to be due to a correlation between the size of the irreversibility in C_p and the magnetization jump approaching the maximum of the dome of phase II.

$CeRu_2Si_2$, by contrast, does not transform into a new state at low temperatures [11]. The similarity in the intensity of the fluctuations in the two systems suggests that while they play a crucial role in driving the system towards instability at H_m, the increased tendency for direct or superexchange between $5f$ orbitals compared to $4f$ orbitals appears to be the decisive factor in whether a new ordered phase actually occurs. The very appearance of ordered phases in $U(Ru, Rh)_2Si_2$, in connection with an isolated nonsymmetry-breaking quantum-critical point (as opposed to one that is symmetry breaking), suggests that the tendency to form new states of matter is ubiquitous to both forms of quantum criticality. Such a finding may have far reaching implications because it introduces the possibility of high temperature superconductivity being connected with a nonsymmetry-breaking quantum-critical end point. This would eliminate the need to attribute the pseudogap regime in the cuprates to a symmetry-breaking order parameter [5,32]. Finally, if it is the exchange between the orbitals that ultimately optimizes conditions for the formation of an ordered phase, this would help to explain the common trend in maximum ordering transition temperatures in progressing from $4f$ to $5f$ to d electrons.

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Note added.—Since submission of this Letter, an analysis of magnetic field orientation-dependent de Haas–van Alphen data has confirmed that nearly localized $5f$ electrons with Γ_5 degrees of freedom contribute to the Fermi liquid properties of URu_2Si_2 [A. V. Silhanek *et al.*, cond-mat/0506384].

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