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Probing strong Kondo disorder with measurements of thermoelectric power

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Measurements of thermoelectric power $S(T)$ on the Kondo disorder system $\mathrm{CePt_4Ge_{12-x}Sb_x}$ are remarkably sensitive to the distribution of Kondo temperatures $P(T_K)$, which develops out of a single Kondo temperature T_K in $\mathrm{CePt_4Ge_{12}}$ and is governed by the degree to which hybridization is disordered. Three distinct $S(T)$ behaviors are observed in concentration regions which coincide with the boundaries of Fermi liquid, non-Fermi liquid, and antiferromagnetically-ordered ground states in this system. In the non-Fermi liquid region, $S(T)/T$ diverges logarithmically with decreasing temperature over nearly one decade in the case of $x = 0.84$.

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Fermi-liquid (FL) instabilities are manifested in non-Fermi liquid (NFL) behavior of the thermodynamic and transport properties and have been the subject of intensive experimental and theoretical studies over the past two decades [1–3]. For many systems, NFL behavior is governed by strong quantum fluctuations from a nearby quantum critical point (QCP) [2–4]; however, other mechanisms can produce NFL behavior in the absence of a QCP. One prominent example occurs when hybridization between localized and itinerant electron states, defined in the context of the Anderson model [5] and characterized by a Kondo temperature T_K, becomes strongly disordered through chemical substitution, leading to a distribution of Kondo temperatures $P(T_K)$. When $P(T_K)$ includes an appreciable number of localized electron sites with $T_K \sim 0$ K, the specific heat divided by temperature diverges [6, 7] as $C(T)/T \sim 1/T_\gamma \log(T_\gamma/T)$ and electrical resistivity [8] is dominated by a contribution $\rho(T) \simeq \rho_0(1 - T/T_\rho)$ where T_γ and T_ρ are characteristic temperatures. Each of these behaviors deviates significantly from the results of FL theory [3] (*i.e.*, $C(T)/T \simeq \gamma$ and $\rho(T) \sim \pm(T/T_F)^2$ where T_F is the Fermi temperature).

Understanding the break down of the FL paradigm and emergence of NFL behavior remains one of the most important problems in strongly correlated electron physics. Recent studies have begun to establish how sensitively measurements of thermoelectric power $S(T)$ probe quantum criticality [9–11]. For example, $S(T)$ can unambiguously distinguish between Kondo breakdown and spin-density wave QCP scenarios [9], and low-temperature $S(T)$ measurements have been performed to study the behaviors of $\mathrm{YbRh_2Si_2}$ and $\mathrm{CeCu_{6-x}Au_x}$ near their QCPs [10, 11]. On the other hand, experimental studies of $S(T)$ on Kondo disorder systems where disorder is introduced through chemical substitution on ligand sites have not yet been performed. This is surprising since Kondo lattice systems exhibit prominent features in $S(T)$ as a result of a many-body resonance that can be split by the crystalline electric field (CEF) and a Kondo resonance in the spectral weight $A(\omega)$ [12–14]; these resonances are governed by hybridization, so the development of $P(T_K)$ in a Kondo disorder system should significantly affect the character of $S(T)$.

The compound $\mathrm{CePt_4Ge_{12}}$ has a FL ground state [15–17] with no ordered phase down to 50 mK [16]. Chemical substitution of Sb for Ge in the system $\mathrm{CePt_4Ge_{12-x}Sb_x}$ produces strongly-disordered hybridization which tunes the system through a region of NFL behavior for $1 \leq x \leq 1.3$, and leads to antiferromagnetic (AFM) order for $x \geq 1.9$ [16]. In this letter, we demonstrate how sensitively measurements of $S(T)$ probe Kondo disorder in $\mathrm{CePt_4Ge_{12-x}Sb_x}$. The character of $S(T)$ evolves dramatically in response to the development of $P(T_K)$ with x such that distinct $S(T)$ behavior is observed within three concentration regions. These regions correspond to the ground states reported in Ref. [16] and indicate significant redistributions of spectral weight associated with the many-body and Kondo resonances upon crossing their boundaries. At low T and for $0.84 \leq x \leq 1.5$, $S(T)/T$ appears to diverge with decreasing T with a NFL form, $S(T)/T \sim 1/T_S \log(T_S/T)$, where $T_S \neq T_\gamma$, in general. Upturns are observed in $S(T)/T$ in response to Kondo disorder which precede analogous upturns in $C(T)/T$, such that their ratio in the limit of $T \to 0$ K is sensitive to the development of $P(T_K)$.

Polycrystalline samples of $\mathrm{CePt_4Ge_{12-x}Sb_x}$ ($0 \leq x \leq 3$) were synthesized as reported elsewhere [17]. Measurements of powder x-ray diffraction (not shown) showed that the samples are nearly phase-pure with minor $\mathrm{PtGe_2}$ and Ge impurity phases. Lattice parameter values agree with results in Ref. [16]. $C(T)$ and $S(T)$ measurements were performed in a PPMS DynaCool. $C(T)$ measurements employed a standard thermal relaxation technique. $S(T)$ was measured by applying a static temperature gradient of $\Delta T/T = 2$ - 5%, measured using two Cernox 1050 thermometers and a Lakeshore340 Temperature Controller. Copper leads were attached to the sample with silver epoxy in a two-wire configuration. The DC thermoelectric voltage was measured using a Keith-

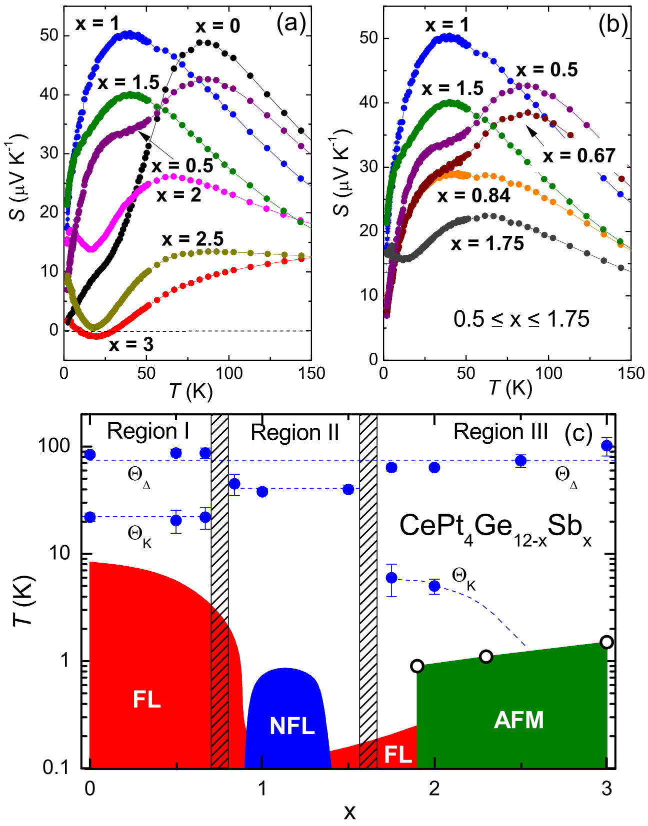

FIG. 1: (Color online) (a) Thermoelectric power S vs. temperature T for $\mathrm{CePt_4Ge_{12-\mathit{x}}Sb_\mathit{x}}$. A dashed line indicates $S(T) = 0$ μV K^{-1}. (b) S vs. T for $0.5 \leq x \leq 1.75$. (c) $T - x$ phase diagram for $\mathrm{CePt_4Ge_{12-\mathit{x}}Sb_\mathit{x}}$. The Fermi liquid, non-Fermi liquid, and antiferromagnetic (AFM) regions, colored red, blue, and green, respectively, were reported in Ref. [16]. The AFM phase boundary should go to zero temperature at a concentration in the range $1.5 < x < 1.9$. Striped bands separate regions corresponding to distinct $S(T)$ behavior. Blue circles represent the maxima of features observed in $S(T)$ at temperatures Θ_K and Θ_Δ (see text). Dashed lines are guides to the eye.

ley 2182 Nanovoltmeter and was corrected for a background contribution arising from thermal/compositional asymmetry in the wires running from the sample to the external electronics at room temperature [18].

A dramatic evolution of $S(T)$ for $\mathrm{CePt_4Ge_{12-\mathit{x}}Sb_\mathit{x}}$ is shown in Figs. 1(a) and (b). For $0 \leq x < 0.84$, a large feature centered near a temperature $\Theta_\Delta \sim 85$ K and a lower temperature feature near $\Theta_K \sim 20$ K are observed. The magnitude of $S(\Theta_K)$ relative to $S(\Theta_\Delta)$ increases with x until $x = 0.84$ when the feature at Θ_Δ is absent. Instead, a solitary feature appears to emerge from the Θ_K feature in the $x = 0.67$ data (see Fig. 1(b)). The data for $x = 1$, 1.5 also exhibit a single, broad feature; its magnitude increases dramatically between $x = 0.84$ and $x = 1$ and subsequently decreases for $x = 1.5$. Between $x = 1.5$ and $x = 1.75$, the behavior of $S(T)$ evolves again so that two features are recovered. A possible shoulder feature near 10 K in $x = 1.5$ data may anticipate this change. This behavior continues with increasing x to the solubility limit [16] near $x = 3$ as the magnitude of $S(T)$ decreases, becoming negative for $x = 3$ over a small temperature range. For $x \geq 2.5$, the maximum at Θ_K is not resolved down to our lowest measured temperatures, so $\Theta_K < 2$ K for these concentrations.

The sign and magnitude of the $4f$ electron contribution to $S(T)$ in clean Ce-based intermetallic compounds are governed by the temperature-dependent evolution of the spectral weight $A(\omega)$ [12–14]. Many-body effects related to hybridization between localized and itinerant electron states (characterized by hybridization matrix element V_{kf}) produce a resonance in $A(\omega)$ that leads to [12] a large feature in $S(T)$ with maximum at $\Theta_\Delta \sim \Delta/2$. Here, Δ is the splitting of the Ce $J = 5/2$ multiplet by the CEF. For $T < \Theta_\Delta$, the emergence of the Kondo resonance in $A(\omega)$ produces a feature in $S(T)$ with maximum at Θ_K (where $\Theta_K = T_K$ in the single-ion impurity limit) [12]. The relative magnitudes of these two features and the characteristic temperature Θ_K depend on how $\Gamma \equiv \pi V_{kf}^2 N(\epsilon_F)$ compares with Δ, where $N(\epsilon_F)$ is the density of electronic states at the Fermi energy [12]. When hybridization is strong (large V_{kf} and T_K) so that $\Gamma/\Delta \geq 2$, the feature at Θ_K will appear as a shoulder on the much larger feature at Θ_Δ or may be entirely absent. As Γ/Δ decreases, $S(\Theta_\Delta)$ decreases and the feature at Θ_K moves to lower temperature. Near $\Gamma/\Delta \sim 1$, the two features are well-separated and $S(T)$ is small and possibly negative over extended temperature ranges [12].

We observe three distinct types of behavior in concentration ranges: $0 \leq x < 0.84$, $0.84 \leq x < 1.75$, and $1.75 \leq x \leq 3$, labeled regions I, II, and III, respectively, in Fig. 1(c) where the $T - x$ phase diagram for $\mathrm{CePt_4Ge_{12-\mathit{x}}Sb_\mathit{x}}$ from Ref. [16] is also displayed. The filled circles indicate Θ_Δ and Θ_K for each concentration. The $S(T)$ data for $x = 0$ are consistent with $\Gamma/\Delta \sim 2$. If we consider only regions I and III and neglect disorder, the evolution of $S(T)$ with x suggests that Γ/Δ continuously decreases to $\Gamma/\Delta \sim 1$ by $x = 3$. This trend is consistent with the expansion of the lattice produced by substituting larger Sb ions for Ge [16], which would tend to decrease Γ/Δ by reducing V_{kf}. However, in contrast to the continuous evolution of $S(T)$ with x we would expect if we could *cleanly* tune Γ/Δ to smaller values without adding disorder [12], there is an abrupt change in the character of $S(T)$ in region II where a single broad feature emerges. A sharp increase in $S(\Theta_K)$, that is particularly evident between $x = 0$ and $x = 0.5$ (see Fig. 1(a)), precedes the crossover to a single-feature character, indicating a dramatic redistribution of spectral weight. The NFL behavior reported [16] to coincide with region II indicates that $P(T_K)$ includes an appreciable number of $T_K = 0$ K sites for $0.84 \leq x < 1.5$ (*i.e.*, strong Kondo disorder). The evolution of the feature at Θ_K for $x < 0.84$ must be sensitive to the development of $P(T_K)$ with x

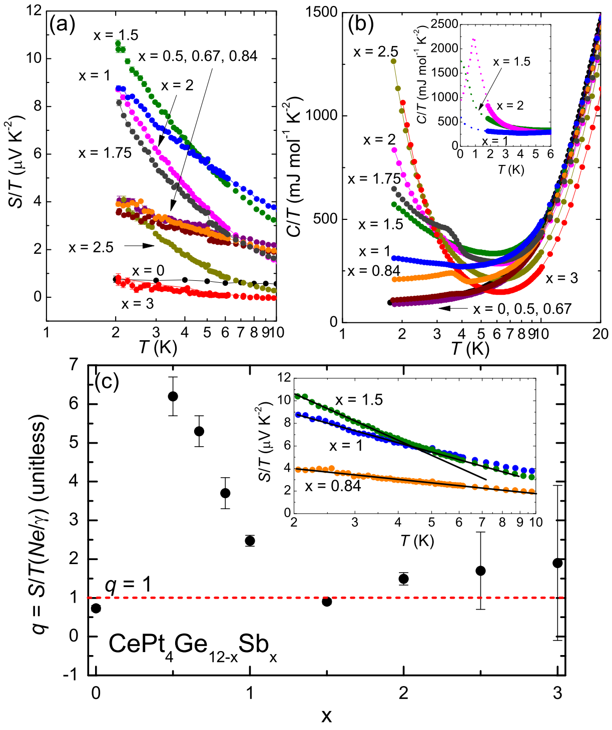

FIG. 2: (Color online) (a) Thermoelectric power $S(T)$ plotted as S/T vs. $\log(T)$ for CePt$_4$Ge$_{12-x}$Sb$_x$. (b) Specific heat $C(T)$ plotted as C/T vs. $\log(T)$. The inset shows low T data from Ref. [16] as dashed lines. (c) q, defined in Eq. 1, plotted as a function of x. The inset emphasizes the logarithmic temperature dependence of S/T for $0.84 \leq x \leq 1.5$ over a limited temperature range.

through its effect on the Kondo resonance in $A(\omega)$. Calculations for a disordered system with two distinct hybridization strengths predict two distinct Θ_K features in $S(T)$ [13]. Extrapolating from this result, a continuous distribution $P(T_K)$ should lead to a broad peak in $S(T)$ formed from many features, each with their own characteristic T_K (and Θ_K) values. Furthermore, the magnitude of this feature should be large since we are probing scattering in a highly-disordered system. This picture is consistent with our results.

The influence of Kondo disorder on $S(T)$ is especially prominent at low T where $S(T)$ is quite large. Stated differently, $S(T)/T$ appears to diverge with decreasing T. In a simple free electron gas, $S(T)/T$ and $C(T)/T$ are temperature-independent for $T << T_F$ [19], and near a QCP, each diverges logarithmically or with a weak power law with decreasing T depending on dimensionality and other details [9, 10]. Given this precedence, it is reasonable to anticipate that $S(T)/T$ might behave similarly to $C(T)/T$ in a Kondo disorder scenario as well. $S(T)/T$ data in Fig. 2(a) and $C(T)/T$ data in Fig. 2(b) share qualitative similarities at low T. The $C(T)/T$ data are consistent with other reported results [16], and diverge for $x \geq 0.84$ with decreasing T. A feature is observed near 4 K in data for $x = 0.84$ and 1.75 that is due to an impurity phase. The upturn in $C(T)/T$ for $x = 1$ is consistent with NFL behavior of the form $C(T)/T \sim 1/T_\gamma \log(T_\gamma/T)$ down to 50 mK [16]. Upturns in $C(T)/T$ for $x \geq 1.5$ either saturate at low T ($x = 1.5$) or are the high T portions of lambda anomalies associated with AFM order ($x \geq 1.9$) as seen in the inset of Fig. 2(b) where dashed lines represent data from Ref. [16].

Inspection of $S(T)/T$ data in Fig. 2(a) suggests that a logarithmic temperature dependence may be present for some concentrations. $S(T)/T$ data for $0.84 \leq x \leq 1.5$ (roughly region II) are displayed in the inset of Fig. 2(c), which are characterized by $S(T)/T \sim 1/T_S \log(T_S/T)$ behavior extending up to ∼10 K for $x = 0.84$ and ∼5.5 K and ∼4 K for $x = 1$ and 1.5, respectively. These observations are consistent with NFL behavior; however, this conclusion would be better supported by data measured to lower temperatures. For example, $C(T)/T \sim 1/T_\gamma \log(T_\gamma/T)$ for $x = 1, 1.3$ from 0.05 K up to only ∼1 K [16]. We note, however, that the upturn in $C(T)/T$ for $x = 1$ at $T > 1$ K also has its origin in the same Kondo-disorder mechanism even though it does not exhibit a logarithmic temperature dependence. Furthermore, though the upturn in $C(T)/T$ for $x = 1.5$ saturates at low T (FL ground state) and lacks a discernable logarithmic temperature dependence [16], its presence indicates a significant level of Kondo disorder. The analogous upturns in $S(T)/T$ data for regions I and II are highly sensitive responses to Kondo disorder. They become prominent starting at $x = 0.5$, which precedes the initial observation of the upturn in $C(T)/T$ for $x = 0.84$. This result emphasizes how sensitive $S(T)$ is to Kondo disorder relative to $C(T)/T$. It also suggests that, while $S(T)/T$ and $C(T)/T$ share similar temperature dependencies, the scales associated with each (*i.e.*, T_S and T_γ in the NFL region) are different in general.

The Kadowaki-Woods and Wilson ratios [20, 21] exhibit universal values for a broad class of strongly correlated electron materials with FL ground states. Behnia *et al.* empirically observed that a ratio of $S(T)/T$ and $C(T)/T$ (Sommerfeld coefficient γ), extrapolated to zero temperature, is also universal for FL states [19]. A free electron gas with energy-independent relaxation times and one itinerant electron per formula unit yields $|q| = 1$ where

$$q = \frac{S}{T}\frac{Ne}{\gamma}, \tag{1}$$

and Avagadro's number N and the electron charge e make q dimensionless [19].

The quantity $q(x)$, as defined in Eq. (1), is plotted in Fig. 2(c). Values for $\gamma = C(T)/T$ were extracted from data in Ref. [16] for $x \geq 1$ and values of $S(T)/T$ were obtained by extrapolating our data to $T = 0$ K linearly. At $x = 0$ and for $x \geq 1.5$, $q \sim 1$ (within error estimates for $x = 2.5, 3$), which is consistent with the FL ground state reported for these concentrations [16]. It may be tempting to interpret strongly $q \neq 1$ values for $0.5 \leq x < 1.5$ as evidence for NFL behavior; however, NFL behavior is only actually observed for $1 \leq x \leq 1.3$ in $C(T)/T$ [16] and possibly $0.84 \leq x < 1.5$ in $S(T)/T$. The rapid increase of $q(x)$ at low x and subsequent decrease for $0.5 \leq x < 1.5$ is a reaction to the upturn in $S(T)/T$ preceding the analogous upturn in $C(T)/T$, with the latter eventually catching up. In this context, $q(x)$ probes the development of Kondo disorder rather than acting as a tool to distinguish FL from NFL ground states. In the NFL region, $q \propto T_\gamma/T_S$ so the decrease in $q(x)$ suggests that T_S and T_γ converge towards a common value. This is plausible since for $x = 1$ we determine $T_\gamma \simeq 24$ K and $T_S \simeq 23$ K. By linearly extrapolating our $S(T)/T$ data to zero temperature, we implicitly assume that no additional energy scales emerge below 2 K that significantly modify the behavior of $S(T)/T$. For example, the dramatic T-dependence of $S(T)/T$ observed in systems like CeAl$_3$ is due to a low-lying energy scale related to Kondo physics, which requires measurements to very low T to meaningfully evaluate $S(T)/T$ in the limit $T \rightarrow 0$ K [19, 22]. In CePt$_4$Ge$_{12-x}$Sb$_x$, however, $C(T)/T$ is well-behaved at low T for most concentrations and the only emerging energy scale is $T_N < 2$ K for $x \geq 1.9$. Therefore, our linear extrapolation is justified for most concentrations. For $x \geq 1.9$, we expect a kink in $S(T)$ near T_N that will probably reduce $S(T)/T$ such that we overestimate the intercept. This would artificially enhance q, which is consistent with Fig. 2(c) where $q > 1$ for $x \geq 1.9$. To account for possible over- or underestimates of the intercept, conservative errors were determined and propagated through in calculations of q.

Thermoelectric power $S(T)$ is a sensitive probe of the distribution of Kondo temperatures $P(T_K)$, which develops in the Kondo disorder system CePt$_4$Ge$_{12-x}$Sb$_x$ from a single T_K at $x = 0$. As hybridization becomes increasingly disordered with x, $S(T)$ evolves so that three distinct behaviors are observed in regions which coincide with the previously-established boundaries of FL, NFL, and AFM ground states. This is particularly interesting when we consider that, while these boundaries were originally determined by performing very low-T specific heat measurements, we could reproduce them with measurements of $S(T)$ at $T > 2$ K. The abrupt crossover from two distinct features to a single feature in $S(T)$ for $0.84 \leq x < 1.5$ coincides with the emergence of NFL behavior, which is produced by very strong Kondo disorder characterized by $P(T_K)$ with an appreciable number of Ce sites with $T_K \sim 0$ K. In the NFL region, $S(T)/T$ appears to diverge logarithmically with decreasing temperature in a manner similar to $C(T)/T$; however, $S(T)$ should be measured at $T < 2$ K to confirm this behavior. The upturn in $S(T)/T$ at low T that develops as a result of Kondo disorder precedes an analogous upturn in $C(T)/T$ such that the ratio of $S(T)/T$ to $C(T)/T$, where each is taken in the limit of zero temperature, is particularly sensitive to the development of $P(T_K)$. These results demonstrate that $S(T)$ is a useful and, heretofore, unappreciated tool for identifying and characterizing Kondo disorder systems. This intrinsic utility of $S(T)$ to study Kondo disorder would be significantly enhanced by models with which data could be compared, and we hope that these results will motivate the development of such models.

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