Comparison of $CeRh_2Si_2$ and $CeRh_{2-x}Ru_xSi_2$ near their Magnetic-Nonmagnetic Boundaries

T. Graf,* J. D. Thompson, M. F. Hundley, R. Movshovich, Z. Fisk,† and D. Mandrus‡
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

R. A. Fisher and N. E. Phillips
Lawrence Berkeley National Laboratory and Department of Chemistry, University of California, Berkeley, California 94270
(Received 2 December 1996)

A zero-temperature magnetic-nonmagnetic phase boundary is accessed in $CeRh_2Si_2$ by application of pressure and in $CeRh_{2-x}Ru_xSi_2$ at ambient pressure for $x \approx 1.0$. A comparison of specific heat and resistivity measurements in the two cases emphasizes the importance of disorder in producing non-Fermi-liquid-like behavior in these as well as in other Ce-based systems. [S0031-9007(97)03104-9]

PACS numbers: 75.40.Cx, 62.50.+p, 71.27.+a, 75.20.Hr

The ground state of a periodic lattice of Kondo impurities is determined by the competition between intersite, Ruderman-Kittel-Kasuya-Yosida (RKKY), and intrasite, Kondo, interactions [1,2]. The balance between these pressure-dependent interactions is set by the magnitude of the exchange parameter J, with RKKY interactions increasing as J^2, and Kondo interactions increasing exponentially with J. Because of these different functional dependences on J, at some critical value J_c there will be a zero-temperature critical point that separates a magnetically ordered phase from one with no long range order, assuming that some other phase transition does not intervene. Fluctuations around this quantum-critical point are expected to lead to non-Fermi-liquid (NFL) temperature dependences of thermodynamic and transport properties [3,4]. Other suggested origins of NFL behavior found in Ce- and U-based Kondo-lattice compounds [5] include local spin fluctuations near an antiferromagnetic instability [6,7], a multichannel Kondo effect [8], and a distribution of Kondo temperatures introduced by crystallographic disorder [9]. Attempts to describe NFL power law and logarithmic dependences of thermodynamic and transport properties by these possible mechanisms have met with varying degrees of success [7–11], and there remains no consensus for the origin of NFL behavior. However, what is common to these systems in which NFL behavior is claimed is the presence of disorder, introduced intentionally by chemical alloying on the f or ligand sites or that is inherent to the material's crystal structure, e.g., Ce_7Ni_3 [12]. In this Letter, we report results of a study in which a zero-temperature critical point in $CeRh_2Si_2$ is accessed in two ways: by application of pressure, which does not introduce disorder, and by chemical substitution of Ru for Rh, which does. The results are qualitatively different. They strongly suggest the important role of disorder in inducing NFL behavior in this system and, by implication, more generally in f-electron NFL systems.

$CeRh_2Si_2$ is an ideal system for this study. Its Néel temperature T_N can be reduced from an ambient pressure value of 35 K to $T = 0$ at a critical pressure $P_c \sim 9$ kbar [13], a pressure readily accessible in specific heat and resistivity measurements. Substitution of Ru for Rh drives T_N to zero in $CeRh_{2-x}Ru_xSi_2$ for $x_c \approx 0.95$ [14]. Measurements reported below were performed on well-characterized $CeRh_2Si_2$ and $CeRh_{2-x}Ru_xSi_2$ ($x = 1.0$) samples prepared by arc melting. Powder x-ray diffraction showed that all samples formed in the $ThCr_2Si_2$ structure with no detectable second phase. Pressure measurements were carried out in Be-Cu pressure cells with AgCl (flourinert) as the pressure-transmitting medium in specific heat (resistivity) experiments. Additional experimental details will be given later [15].

The inset in Fig. 1 shows the magnetic specific heat $C_m(T)$ divided by temperature for $CeRh_2Si_2$ at ambient pressure. A sharp anomaly, peaked near 35 K, signals the onset of magnetic order that is also found at this temperature in magnetic susceptibility and resistivity measurements. The magnetic entropy, represented by the solid curve, crosses the dotted horizontal line corresponding to $S_m = R \ln 2$ at a temperature just above T_N, implying that magnetic order develops in a ground-state doublet. In the absence of magnetic order, we can estimate the specific heat Sommerfeld coefficient γ from the Anderson-impurity relationship $\gamma = (N - 1)\pi R/6T_K$, where N is the ground-state degeneracy and R is the gas constant. Taking $T_K = 33$ K from quasielastic neutron scattering experiments [17] at $T \geq T_N$ and $N = 2$, we obtain $\gamma = 130$ mJ/mole K^2, much greater than the experimental value, 22.8 mJ/mole K^2 (see Fig. 1). This large reduction in γ in the ordered state is found commonly in Ce-based magnets with nearly full-moment ordering and may be attributed [18] to the existence of a large internal magnetic field that quenches, at least partially, Kondo-like spin fluctuations.

Figure 1 also shows the effect of pressure on C_m/T for $CeRh_2Si_2$ at $T \leq 10$ K. With the application of pressure, there is a qualitative increase in C_m/T at all temperatures, but an uncertainty of 0.5% in the heat capacity of the pressure cell limits a detailed interpretation of $C_m(T)$ for temperatures near and above 10 K. However, a specific heat anomaly with a magnitude of 10% or more of the $P = 0$ anomaly would be clearly observable.

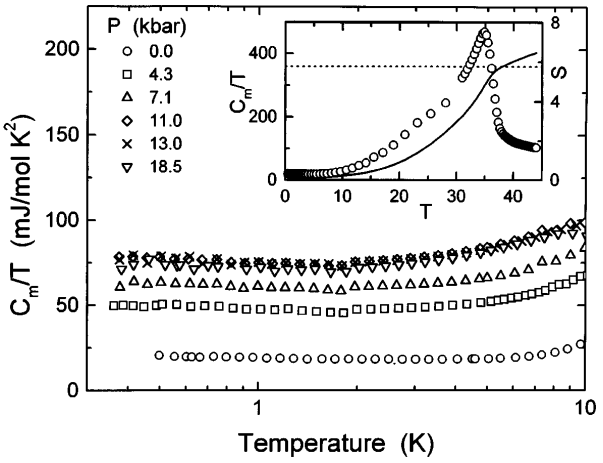

FIG. 1. Magnetic specific heat C_m divided by temperature as a function of temperature on a logarithimic scale for $CeRh_2Si_2$ at various pressures. The lattice specific heat of $CeRh_2Si_2$ was approximated by that of $LaRhRuSi_2$ [16] and subtracted from the total specific heat to obtain C_m. The inset is a plot of C_m/T vs T for $CeRh_2Si_2$ at ambient pressure—open circles. The solid curve is the magnetic entropy, calculated as the integral of $C_m(T)/T$, and the dotted horizontal line corresponds to $S_m = R \ln 2$.

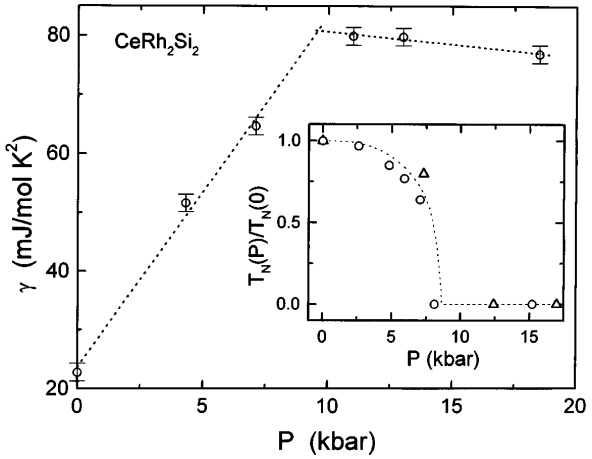

FIG. 2. Linear-in-temperature specific heat coefficient γ of $CeRh_2Si_2$ as a function of pressure. The inset is a plot of $T_N(P)$ normalized to its $P = 0$ value for two different samples. In both cases, the dotted constructions are guides to the eye.

The absence of a phase transition in these data can be understood from the pressure dependence of T_N established by resistivity measurements and shown in the inset of Fig. 2: For pressures less than 7.1 kbar, $T_N(P) \geq 0.75T_N(0) = 26.2$ K, which is outside the temperature range of pressure-dependent specific heat measurements; for $P \geq 11.0$ kbar, $T_N = 0$. Overall, C_m/T data shown in Fig. 1 are fully consistent with the $T_N(P)$ phase diagram determined resistively.

In direct contrast with the behavior of nonordering Ce heavy-fermion systems, in which γ decreases with pressure [19], γ increases initially as pressure is applied, which is shown in Figs. 1 and 2. However, for higher pressures, γ does decrease, approximately linearly, with increasing pressure. The linear-in-pressure constructions in Fig. 2 show that the crossover from $\partial\gamma/\partial P > 0$ to $\partial\gamma/\partial P < 0$ occurs very near P_c. Qualitatively, this behavior of $\gamma(P)$ can be understood on the basis of Doniach's model [2] for competing Kondo and RKKY interactions. With increasing pressure, the balance between Kondo and RKKY interactions shifts in favor of increasing dominance of Kondo-spin compensation of the localized $4f$ moments, redistributing magnetic entropy both to higher temperatures (because T_K increases with pressure) and from localized degrees of freedom to Kondo-like spin fluctuations. It is this latter process that produces the initial increase in γ which is allowed because the internal magnetic field is also suppressed through the Kondo effect. Once the ground state is paramagnetic ($P > P_c$), γ decreases as in nonordering Ce heavy-fermion compounds.

Sufficiently near P_c, quantum-critical fluctuations should dominate the low-temperature specific heat, producing a logarithmic or stronger divergence of C_m/T and very large values of this ratio [3]. Neither of these effects are found in our measurements. Inspection of the data in Fig. 1 shows the absence of any significant temperature dependence of C_m/T at low temperatures. Therefore, we conclude that there is no evidence in these data for non-Fermi-liquid behavior. This conclusion is supported as well by our resistivity measurements (not shown) that give, for $T \leq 10$ K, $\rho \propto T^\beta$ with $\beta = 2.80 \pm 0.5$ at $P = 7.3$ kbar and $\beta = 2.03 \pm 0.01$ at $P = 12.4$ kbar.

The T_N phase boundary is very steep as P approaches P_c, unlike that for $CeCu_{6-x}Au_x$ with $x = 0.2$ and 0.3 [11,20] but more like Ce_7Ni_3 [10]. Taking $P_c = 9$ kbar for $CeRh_2Si_2$, we have specific heat data at $0.79P_c$ and $1.22P_c$. However, $C_m/T \propto -\ln T$ in Ce_7Ni_3 for $P \leq 1.5P_c$ and in $CeCu_{5.8}Au_{0.2}$ to a least $P = 1.2P_c$, in both cases remarkably far from the critical point. If NFL signatures arise from quantum or local spin fluctuations in those cases, they should be observed clearly in our data as well, but they are not. A possible explanation for the lack of a well-defined logarithmic temperature dependence of C_m/T in $CeRh_2Si_2$ is that the transition is first order near P_c. However, there is no indication of a first-order transition in the specific heat data. We also have looked for hysteretic behavior in $T_N(P)$ near P_c by resistivity measurements, and within uncertainties in determining T_N (± 1 K) and P (± 0.5 kbar), there is no evidence for hysteresis that might be taken as indicative of a first-order transition.

It is instructive to compare these pressure results to those obtained at ambient pressure when $CeRh_2Si_2$ is alloyed with Ru. Substituting Ru in $CeRh_{2-x}Ru_xSi_2$ initially suppresses T_N rapidly to a plateau, where $T_N \sim 11$ K (for $0.2 < x < 0.8$). With additional Ru substitution, T_N drops abruptly to zero at $x_c \approx 0.95$ [14], similar to the drop of T_N near P_c in $CeRh_2Si_2$. The results of specific heat and susceptibility measurements are shown in Fig. 3 for one representative sample with nominal $x = 1.0$ [21]. For this

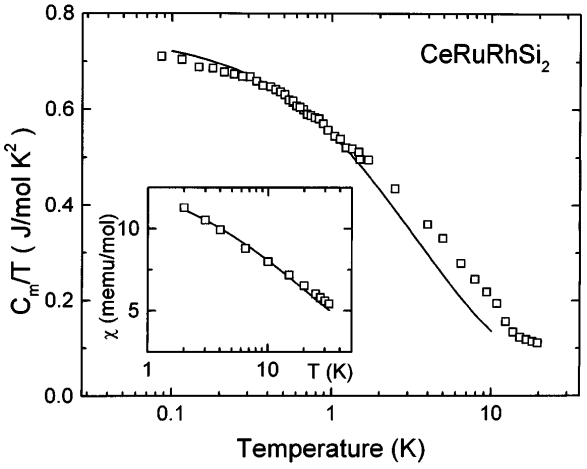

FIG. 3. Magnetic specific heat C_m divided by temperature versus the logarithm of temperature for $CeRhRuSi_2$. The solid line is calculated as described in the text. The inset plots the susceptibility of $CeRhRuSi_2$ versus log$T$. The solid line is a fit of the Kondo disorder model to the data for $2 \leq T \leq 30$ K.

sample, C_m/T increases logarithmically from ~11 K to near 1 K before rolling over to an approximately constant value of ~700 mJ/mole K^2 for $T \leq 0.2$ K. Interestingly, a linear extrapolation of C_m/T vs T^2 from above 15 K to $T = 0$ gives $\gamma(T = 0) = 130$ mJ/mole K^2, a value remarkably close to our estimate of γ from the neutron quasielastic linewidth of $CeRh_2Si_2$ at $T \geq T_N$. As shown in the inset to Fig. 3, $\chi \propto -\ln T$ for $2 \leq T \leq 30$ K. Although there is some evidence in C_m/T and χ for minor sample inhomogeneity, these data are generally consistent with NFL behavior in an interval spanning at least one decade in temperature above ~1 K. However, specific heat measurements below 1 K suggest that the NFL behavior does not persist in the ground state of $CeRhRuSi_2$ but that C_m/T approaches more conventional Fermi-liquid behavior at the lowest temperatures. This is corroborated by resistivity measurements (not shown) that find $\rho = \rho_0 + AT^2$ for $0.04 \leq T \leq 0.20$ K, where $\rho_0 = 83\ \mu\Omega$ cm and $A = 24\ \mu\Omega$ cm/K^2. The large T^2 coefficient is also consistent with the large $T \to 0$ Sommerfeld coefficient.

There are two notable differences between conditions under which NFL behavior is found in $CeRhRuSi_2$ and those that fail to show NFL signatures in $CeRh_2Si_2$. The first difference is the nearness to a $T = 0$ critical point. Defining nearness as $\Delta = |\delta - \delta_c|/\delta_c$, where δ is pressure in the case of $CeRh_2Si_2$ or x in $CeRh_{2-x}Ru_xSi_2$, then $\Delta \geq 0.2$ for $CeRh_2Si_2$ and $\Delta = 0.05$ for $CeRh_{2-x}Ru_xSi_2$. The second difference is that $CeRh_2Si_2$ is cystallographically ordered, whereas alloying with Ru introduces disorder. Recent model calculations [22] of a disordered Anderson lattice demonstrate that NFL behavior is a robust feature, provided that disorder is sufficient to produce a distribution of Kondo temperatures, which includes $T_K \to 0$, and that RKKY interactions are negligible. Because this model is related closely to the phenomenological approach used by Bernal *et al.* [9], we follow Ref. [9] by assuming that alloying with Ru produces a distribution of Kondo temperatures through a Gaussian distribution $P(\lambda)$, where λ is defined by the relationship $T_K(\lambda) = E_F \exp(-1/\lambda)$. The average value of χ or C_m is given by

$$\langle X \rangle = \int_0^\infty P(T_K) X(H, T; T_K) dT_K \,. \qquad (1)$$

When X is the susceptibility, we take $X(H, T; T_K) = g\mu_B J B_J(x)/H$, with the argument of Brillouin function B_J given by $x \equiv g\mu_B JH/k_B(T + \sqrt{2}\,T_K)$; for specific heat, we assume the resonant-level model for a Kondo impurity (Eq. 6 of Ref. [23]). Because the ground state is a crystal-field doublet, we use expressions for a spin-$\frac{1}{2}$ impurity in both cases, and set $g = 2$ and $E_F = 1$ eV.

A two parameter fit (mean value of λ and width of the Gaussian distribution $\Delta\lambda$) to $\chi(T)$ data is shown by the solid line in the inset in Fig. 3. Using this same distribution ($\lambda_{\text{mean}} = 0.175$ and $\Delta\lambda = 0.021$), we then *calculate* the temperature-dependent specific heat. The calculated curve agreed reasonably well with the observed T dependence but fell uniformly below the measured curve. The magnitudes of the calculated and measured curves could be reconciled, as shown by the solid line in Fig. 3, by simply redefining the Kondo temperature in the Schotte and Schotte model [23] as $T_K \to aT_K$, where $a = 0.65$. This is not unreasonable, given the qualitative definition of T_K in the expressions for χ and C_m. Given that there are no adjustable parameters in the distribution function $P(\lambda)$ used to calculate $C_m(T)$, the model of disorder provides a relatively good description of the data [24]. The mean T_K's obtained from these procedures are 32.4 K for χ and 21.1 K for C_m, both close to the spin-fluctuation temperature derived from quasielastic neutron scattering in $CeRh_2Si_2$. The width of the Gaussian distribution in λ is $0.12\lambda_{\text{mean}}$ and, consequently, $P(T_K)$ falls rapidly to small values as $T_K \to 0$. That is, the ligand disorder in $CeRhRuSi_2$ is not sufficient to give $P(T_K)$ enough weight at small T_K to produce NFL behavior as $T \to 0$, and thereby allows Fermi-liquid temperature dependences in C_m/T and ρ to emerge at temperatures well below 1 K.

The model of Miranda *et al.* [22] predicts $\rho \propto -bT$ in the limit of strong disorder, contrary to our observations at very low temperatures. Therefore, the NFL behavior at $T \geq 1$ K and Fermi-liquid behavior at $T \ll 1$ K may be understood as a consequence of "moderate" disorder [25] which produces a distribution of Kondo temperatures that cuts off at some low but finite T_K which, in turn, sets the scale ($T_K \approx 6$ K) for $\gamma(T \to 0)$ and T^2 coefficient of resistivity. In the absence of intersite interactions, the Gaussian distribution $P(\lambda)$ would always have finite weight as $T_K \to 0$ and, consequently, a NFL ground state would be expected. In analogy to conventional heavy-fermion system, we speculate that this cutoff arises from the competition between intersite (RKKY) interactions, which may be weakened by disorder, and the distribution of Kondo interactions. Any complete model

of a disordered Anderson lattice must include intersite, as well as intrasite, interactions before a quantitative test of this model is possible.

The contrast in temperature dependences of C_m/T, between $CeRh_2Si_2$ near P_c and $CeRh_{2-x}Ru_xSi_2$ near x_c, is striking. We find no evidence for non-Fermi-liquid behavior in the specific heat or resistivity of $CeRh_2Si_2$ near its $T = 0$ magnetic-nonmagnetic boundary when this boundary is accessed by application of pressure. Comparisons to $CeCu_{6-x}Au_x$ and Ce_7Ni_3 indicate that NFL behavior should have been observed in our data if, in those cases, NFL signatures were due to quantum or local spin fluctuations. This raises the possibility that disorder in $CeCu_{6-x}Au_x$ and Ce_7Ni_3 plays a role in producing $C_m/T \propto -\ln T$ behavior near their magnetic-nonmagnetic boundaries. It is noteworthy that the residual resistivity of $CeCu_{5.9}Au_{0.1}$, which is just at the magnetic-nonmagnetic boundary in this system at $P = 0$, and Ce_7Ni_3 near P_c is comparable to that found in $CeRhRuSi_2$. Although by some measure $CeRhRuSi_2$ is closer to a $T = 0$ critical point than $CeRh_2Si_2$ under pressure, which might contribute to the different low temperature behaviors [26], Kondo disorder in $CeRhRuSi_2$ is clearly a significant factor in producing logarithmic divergences of C_m/T and χ over a large low-temperature interval.

We thank M. Continentino and E. Miranda for helpful discussions, and J. L. Smith for preparing a $CeRhRuSi_2$ sample. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy, and work at Lawrence Berkeley National Laboratory was supported by the Director, Office of Basic Energy Research, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC03-76SF00098.

*Present address: Eidgenoessische Technische Hochschule, Zurich, Switzerland.

†Permanent address: National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306.

‡Permanent address: Oak Ridge National Laboratory, Oak Ridge, TN 37831.

[1] See, for example, N. Grewe and F. Steglich, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, Amsterdam, 1991), Vol. 14, p. 343.

[2] S. Doniach, in *Valence Instabilities and Related Narrow Band Phenomena,* edited by R. D. Parks (Plenum, New York, 1977), p. 169.

[3] M. A. Continentino, Phys. Rep. **239**, 179 (1994); M. A. Continentino, Z. Phys. B **101**, 197 (1996).

[4] A. J. Millis, Phys. Rev. B **48**, 7183 (1993); U. Züliche and A. J. Millis, Phys. Rev. B **51**, 8996 (1995).

[5] See, for example, H. v. Löhneysen, Physica (Amsterdam) **206B–207B**, 101 (1995); M. B. Maple *et al.,* J. Low Temp. Phys. **95**, 225 (1994).

[6] T. Moriya and T. Takimoto, J. Phys. Soc. Jpn. **64**, 960 (1995).

[7] S. Kambe *et al.,* J. Phys. Soc. Jpn. **65**, 3294 (1996).

[8] D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987); A. M. Tsvelich, J. Phys. Condens. Matter **2**, 2833 (1990); C. Seaman *et al.,* Phys. Rev. Lett. **67**, 2882 (1991).

[9] O. O. Bernal, D. E. MacLaughlin, H. G. Lukefar, and B. Andraka, Phys. Rev. Lett. **75**, 2023 (1995).

[10] K. Umeo, H. Kadomatsu, and T. Takabatake, J. Phys. Condens. Matter **48**, 9743 (1996).

[11] H. v. Löhneysen *et al.,* Physica B (Amsterdam) (to be published).

[12] K. Umeo, H. Kadomatsu, and T. Takabatake, Phys. Rev. B **54**, 1 (1996).

[13] J. D. Thompson, R. D. Parks, and H. A. Borges, J. Magn. Magn. Mater. **54–57**, 377 (1986).

[14] S. Kawarazaki *et al.,* Physica (Amsterdam) **206B–207B**, 298 (1995).

[15] T. Graf *et al.,* (unpublished).

[16] R. Calemczuk, J. Magn. Magn. Mater. **90–91**, 477 (1990).

[17] A. Severing, E. Holland-Moritz, and B. Frick, Phys. Rev. B **39**, 4164 (1989).

[18] Z. Fisk, J. D. Thompson, and H. R. Ott, J. Magn. Magn. Mater. **76–77**, 637 (1988).

[19] See, for example, J. D. Thompson and J. M. Lawrence, in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 19–Lanthanides/Actinides: Physics II,* eds. K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (Elsevier, Amsterdam, 1994) p. 383.

[20] B. Bogenberger and H. v. Löhneysen, Phys. Rev. Lett. **74**, 1016 (1995).

[21] The temperature dependence and magnitude of the specific heat are highly reproducible among the various samples and agree well with measurements by Lloret *et al.* [J. Magn. Magn. Mater. **63–64**, 85 (1987)]. However, the susceptibility of some samples varies below ~5 K, which may be due to crystalline anisotropy and/or trace amounts of impurity phases.

[22] E. Miranda, V. Dobrosavljevic, and G. Kotliar, Phys. Rev. Lett. **78**, 290 (1997).

[23] K. D. Schotte and U. Schotte, Phys. Lett. **55A**, 38 (1975).

[24] The magnetic field dependence of C_m/T is also consistent with this model. Details of these measurements will be published elsewhere. Though not discussed in the text, we have also attempted to fit C_m/T to the local spin fluctuation model [6]. A fit was not possible using two adjustable parameters, Y_0 and T_0.

[25] Ruthenium hybridizes more strongly than Rh with cerium's f electron [D. D. Koelling, B. D. Dunlap, and G. W. Crabtree, Phys. Rev. B **31**, 4966 (1985); A. L. Cornelius and J. S. Schilling, Phys. Rev. B **49**, 3955 (1994)], but the f-d hybridization matrix element in $CeRu_2Si_2$ is estimated to be only about 17% larger than in $CeRh_2Si_2$ [T. Endstra, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. B **48**, 9595 (1993)]. Consequently, we would not expect strong disorder effects.

[26] NFL behavior is less pronounced in $CeRh_{0.8}Ru_{1.2}Si_2$, i.e., $\Delta = 0.2$, but χ and C_m/T still exhibit $-\ln T$ dependences over a limited low temperature interval and C_m/T approaches 500 mJ/mole K^2 as $T \to 0$.