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Cerium Heavy-Fermion Compounds Near Their $T = 0$ Magnetic-Non-Magnetic Boundary

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Measurements of the temperature-dependent specific heat and thermal expansion coefficient near a $T = 0$ magnetic-non-magnetic boundary, accessed in CeRh_2Si_2 by application of pressure and in $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$ at ambient pressure by chemical substitution, emphasize the role of disorder in producing non-Fermi-liquid behavior. Interestingly, superconductivity also develops near this boundary in some crystallographically-ordered Ce-based heavy-fermion compounds.

[$\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$, specific heat, thermal expansion, susceptibility, non-Fermi-liquid]

1. Introduction

The study of correlated-electron materials near a zero-temperature magnetic-non-magnetic boundary is intrinsically interesting both experimentally and theoretically. Within the past few years, special attention has been drawn to Kondo-lattice/heavy-fermion materials in this limit. Observation of logarithmic or unusual power-law temperature dependences of thermodynamic and transport properties have suggested a non-Fermi-liquid (NFL) groundstate in several Ce- and U-based Kondo-lattice systems in which a $T = 0$ magnetic-non-magnetic boundary has been accessed by application of pressure or by chemical substitutions.[1] These findings have led to several theoretical proposals for the origin of NFL behavior, including quantum-critical fluctuations [2], a multichannel Kondo effect [3], local spin fluctuations near an antiferromagnetic instability [4], and a distribution of Kondo temperatures introduced by crystallographic disorder with associated hybridization disorder [5,6]. Attempts to describe NFL behavior by these models have met with varying degrees of success, and no consensus has emerged for the origin of these effects. However, many of the materials in which NFL behavior has been observed contain some form of disorder, either produced by chemical substitution on f or ligand sites or that which is intrinsic to the material's crystal structure.

Comparably interesting has been the observation of superconductivity that develops in some Ce-based Kondo-lattice systems as their magnetic-non-magnetic boundary is driven toward $T = 0$ by application of pressure. Materials (and critical pressures P_c) where this phenomenon has been found include: CeCu_2Ge_2 (~ 7.7 GPa) [7], CePd_2Si_2 (~ 2.7 GPa) [8], CeRh_2Si_2 (~ 0.9 GPa) [9], CeNi_2Ge_2 (~ 1.5 GPa) [10] and possibly CeCu_2 (~ 6.0 GPa) [11]. This pressure-induced superconductivity is not always reproducible but appears to depend sensitively on sample "quality". Although what precisely is meant by "quality" remains to be determined, there seems to be a correlation between lower residual resistivity and the appearance of superconductivity [12]. Variations in residual resistivity could come from crystallographic imperfections

and/or fluctuations associated with proximity to a magnetic transition, but, again, this needs to be established. In any event, the development of superconductivity near a pressure-induced magnetic-non-magnetic boundary suggests that Cooper pairing may be mediated by some form of magnetic fluctuations and, in analogy to other heavy-fermion superconductors, that the superconductivity is unconventional. Notably, superconductivity has not been found in those materials whose $T = 0$ magnetic-non-magnetic boundary has been accessed by partial substitutions on either the f or ligand sites.

CeRh_2Si_2 is a Kondo-lattice system whose Néel temperature ($T_N \approx 35$ K) can be driven to zero at $P_c \approx 0.9$ GPa [13] or at atmospheric pressure by substituting Ru for Rh[14]. In the following, we compare the temperature dependence of physical properties of these materials near their respective $T = 0$ magnetic-non-magnetic boundaries.

2. Experimental

Polycrystalline samples of CeRh_2Si_2 and $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$ ($x \approx 1$) were prepared by arc melting in an inert atmosphere. In the case of $\text{CeRh}_{0.96}\text{Ru}_{1.04}\text{Si}_2$, sufficient grain growth on the surface of the arc-melted button allowed a small single crystal to be mechanically removed for magnetic susceptibility measurements. Powder x-ray diffraction on all samples showed them to be single-phase with the ThCr_2Si_2 structure. However, specific heat measurements on Ru-doped samples revealed weak anomalies near 5 and 11 K for $x = 1.04$ and 1.0, respectively. In view of the magnetic phase diagram for $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$ [14], these are consistent with the presence of less than 1 mole-percent of slightly Ru-deficient second phase. Specific heat (thermal expansion) measurements on CeRh_2Si_2 under pressure were performed in a Be-Cu clamp with AgCl (Fluorinert) as the pressure-transmitting medium. Thermal expansion measurements at ambient pressure were obtained with a high resolution ($\Delta l/l \approx 10^{-8}$) capacitance dilatometer and those as a function of pressure with a strain-gauge technique [15].

3. Results

Figure 1 shows the magnetic specific heat C_m divided by temperature for CeRh_2Si_2 at pressures below and above the critical pressure P_c required to suppress its Néel temperature to zero. For pressures sufficiently close to P_c , quantum-critical fluctuations should produce a logarithmic or stronger divergence of C_m/T at low temperatures [2,4]; however, these data show no significant temperature dependence below a few Kelvins. It is possible that data have not been acquired sufficiently near the $T = 0$ magnetic-non-magnetic boundary to observe NFL behavior. Taking $|P/P_c - 1| = \Delta$ as a measure of nearness to the quantum-critical point, then $\Delta \geq 0.2$ for the specific data in Fig. 1. For $P/P_c = 0.79$, $T_M(0.79)$ is approximately 25 K and thus $T_M(0.79)/T_M(0) \approx 0.7$. [13,16] By this measure, data at $P/P_c = 0.79$ are relatively far from a critical point, and the absence of NFL behavior is not surprising.

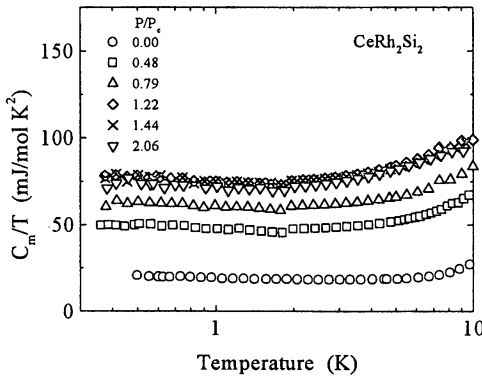


Fig. 1. Magnetic specific heat C_m divided by temperature versus temperature on a logarithmic scale for CeRh_2Si_2 at various pressures P normalized by the critical pressure P_c . The lattice specific heat of CeRh_2Si_2 was approximated by that of LaRhRuSi_2 and subtracted from the total specific heat to obtain C_m .

This issue of proximity to the $T = 0$ transition has been addressed more carefully by thermal expansion measurements. Commonly, properties of Kondo-lattice/heavy-fermion materials are analyzed assuming that the electronic contribution to their free energy scales with a single volume-dependent characteristic energy scale, often associated with the Kondo temperature T_K . [17] With this assumption, the correlated-electron contribution to the volume-thermal expansion coefficient β is related to the specific heat by $\beta = \Gamma \kappa C_m/V$, where κ is the compressibility, V is the volume and Γ is the electronic Grüneisen parameter. If Γ and κ are only weakly affected by quantum-critical fluctuations, then β should exhibit approximately the same temperature dependence as C_m .

Figure 2 shows βT versus temperature on a logarithmic scale for CeRh_2Si_2 at pressures relatively nearer to P_c . For $P/P_c = 0.72$ and 0.89 , large negative anomalies appear at $T_N(P)$. This behavior is expected on the basis of Ehrenfest's relationship and the observed steep decrease in T_N as P approaches P_c . [13,16] For $T > T_N(P)$, βT is positive and close to the curve obtained at $P/P_c = 1.09$. Rather interesting are data obtained closest to the critical point. Here, βT begins to

decrease below about 10 K and appears to diverge approximately logarithmically with decreasing temperatures. If this divergence were due to NFL behavior, it would require that the Grüneisen parameter be negative in this regime. Except for possibly CeAl_3 at very low temperatures, the electronic Grüneisen parameter of Ce-based heavy-fermion materials is positive. [17] Consequently, a negative Γ for CeRh_2Si_2 would be a very unusual situation and, additionally, appears to conflict with results, discussed below, for $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$.

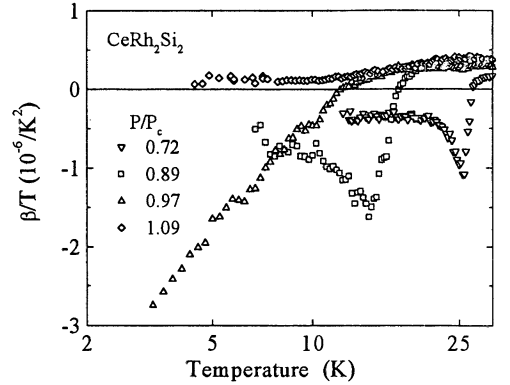


Fig. 2. Volume-thermal expansion coefficient β divided by temperature as a function of temperature on a logarithmic scale for CeRh_2Si_2 at various pressure P normalized by the critical pressure P_c . We have assumed that β is equal to three times the measured linear-expansion coefficient even though the material is tetragonal. Note the absence of a divergence in βT for $P/P_c = 1.09$.

An alternative interpretation of this curve for $P/P_c = 0.97$ is that the decrease in βT beginning near 10 K reflects the approach to a magnetic transition below 3 K. In this case, the transition would have to be exceedingly broad, with a width greater than 7 K, which is not the case at lower pressures. Near P_c , $\partial T_N/\partial P \approx -5.5$ K/GPa for CeRh_2Si_2 . For the transition to extend from roughly 10 to 3 K would imply a pressure gradient $\Delta P \approx 0.12$ GPa in the pressure clamp, if all the broadening were due to non-hydrostaticity. Careful measurements in this clamp on highly stress-dependent superconducting transitions indicated that the maximum pressure gradient is less than 0.01 GPa, or equivalently 10 MPa at a pressure of 1.0 GPa ($\approx P_c$). [18] Even if the relative change in T_N near P_c were underestimated by a factor of two, it seems unlikely that a pressure gradient in the clamp could account for the unusual temperature dependence of βT at $P/P_c = 0.97$. Presently we have no clear understanding of this result, but additional measurements, e.g. thermal expansion to lower temperatures and specific heat at pressures closer to P_c , should be informative.

It is interesting to compare specific heat and thermal expansion measurements on CeRh_2Si_2 under pressure to those obtained at ambient pressure when the CeRh_2Si_2 is alloyed with Ru. Substituting Ru for Rh in $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$ initially depresses T_N rapidly to a plateau where, for $0.2 < x < 0.8$, T_N is about 11 K. With additional Ru, T_N drops abruptly to zero at a critical Ru concentration $x_c \approx 0.95$. [14] Magnetic susceptibility χ and

specific heat measurements on a polycrystalline sample with $x \approx 1.0$ show a NFL-like logarithmic increase in χ and $C_m T$ over an interval spanning more than one decade in temperature above 1 K.[16] However, this NFL behavior does not persist in the ground state of CeRhRuSi₂; instead, $C_m T$ approaches a large, nearly temperature-independent value as T goes to zero, typical of a strongly correlated Fermi liquid. The temperature dependence and magnitude of both χ and C_m could be interpreted consistently assuming that crystallographic disorder introduced by Ru substitution produced a moderately narrow Gaussian distribution of Kondo temperatures around a mean value of about 30 K.[16]

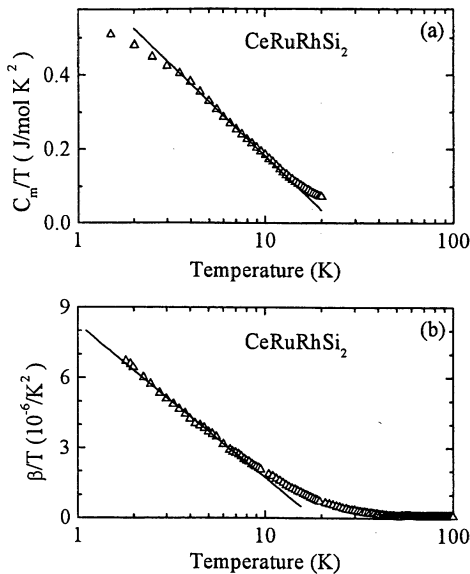


Fig. 3.(a) Magnetic specific heat divided by temperature versus temperature on a logarithmic scale for CeRhRuSi₂ at atmospheric pressure. (b) Volume-thermal expansion coefficient divided by temperature versus temperature on a logarithmic scale. Solid lines are guides to the eye. Note that $C_m T$ and βT both diverge logarithmically over approximately the same temperature interval.

Figure 3 compares the temperature dependence of $C_m T$ and βT for a polycrystalline sample with $x \approx 1.0$. (We have assumed that the volume-thermal expansion coefficient is equal to three times the measured linear coefficient, even though the crystal structure is tetragonal. This assumption should not strongly influence the temperature dependence shown, but probably does affect the quantitative magnitude of β .) As expected from the thermodynamic relationship between β and C_m given earlier, βT increases logarithmically with decreasing temperature over essentially the same temperature interval where $C_m T \propto -\ln T$. The ratio $\beta C_m \propto \Gamma$ is weakly temperature dependent for $1 < T < 10$ K, which can be accounted for [19] semiquantitatively if the distribution of Kondo temperatures also influences Γ . The divergence of βT for CeRh_{2-x}Ru_xSi₂ near its $T = 0$ magnetic-non-magnetic boundary contrasts strongly with results for CeRh₂Si₂.

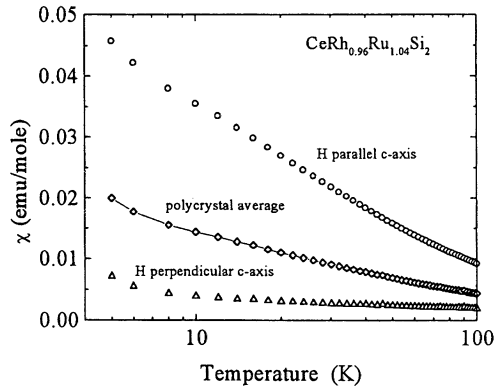


Fig. 4. Magnetic susceptibility of CeRh_{0.96}Ru_{1.04}Si₂ for a 1 kOe field applied parallel (circles) and perpendicular (triangles) to its c-axis. Connected diamonds are a polycrystalline average of the two other data sets. All three sets of data are proportional to $-\ln T$ over the interval $\sim 5 \leq T \leq 50$ K.

Because the Kondo effect arises from hybridization of conduction electrons with a local f-moment, spatial variations in the hybridization matrix element, and correspondingly in T_K , should produce a NFL-temperature dependence in potentially anisotropic physical properties of a disordered system, such as the magnetic susceptibility in CeRh_{2-x}Ru_xSi₂. Figure 4 gives the temperature dependence of χ for a magnetic field applied parallel and perpendicular to the c-axis of a small crystal of CeRh_{0.96}Ru_{1.04}Si₂. The specific heat of this material is identical to that shown in Fig. 3(a) for CeRhRuSi₂. Although there is large anisotropy in the magnitude of χ , both orientations show $-\ln T$ dependence in the range $5 \leq T \leq 50$ K. The weak upturn at low temperatures is sample dependent, suggesting that it arises from trace impurities. A polycrystalline average of these data agrees well with that found earlier [16] on polycrystal CeRhRuSi₂. The somewhat larger low-temperature value of χ_{ave} , compared to CeRhRuSi₂, improves agreement [16] between the mean Kondo temperatures derived by fitting the Kondo-disorder model [5] to χ and $C_m T$.

4. Discussion

As discussed elsewhere in these proceedings [20], there is growing evidence for NFL behavior in Ce-based materials near their $T = 0$ magnetic-non-magnetic boundary. However, except for indications of departure from a Fermi-liquid-like quadratic temperature dependence of the low-temperature resistivity ρ in CePd₂Si₂ [8] and CeNi₂Ge₂ [10,21], there remains no unequivocal evidence for NFL behavior in crystallographically ordered Ce-compounds whose $T = 0$ boundary has been accessed by pressure. CeRh₂Si₂ is no exception. The NFL-like $\rho \propto AT^n$ ($1.1 < n < 1.6$) found in CePd₂Si₂ and CeNi₂Ge₂ also appears to depend sensitively on the magnitude of the residual resistivity ρ_0 and/or crystallographic direction. For example, a CePd₂Si₂ sample with a modestly large $\rho_0 \approx 20 \mu\Omega\text{cm}$ gives $\rho \propto AT^2$ near the $T = 0$ boundary [12] in contrast to $\rho \propto T^{1.2}$ in a sample with $\rho_0 \approx 5 \mu\Omega\text{cm}$ [8], and the c-axis resistivity of CeNi₂Ge₂ increases at T^2 at ambient and high pressures [22] but

reports [10,21] on polycrystalline samples find $\rho \sim T^{1.6}$. What relationship, if any, there is between the existence of NFL-like behavior in these (and isostructural) compounds and the appearance or absence of superconductivity near the $T = 0$ magnetic-non-magnetic boundary is an outstanding question whose answer may provide a fundamental clue to the origin of superconductivity in heavy-fermion compounds in general.

In contrast to well-ordered compounds, there is ample evidence for NFL-like thermodynamic and transport properties in systems whose $T = 0$ magnetic-non-magnetic boundary has been reached by chemical substitutions. The absence of superconductivity in these materials is not surprising because the chemical (and associated hybridization) disorder introduces both elastic and inelastic scattering that would be detrimental to superconductivity, especially if it were unconventional. Although no consensus has emerged for a common interpretation of the origin of NFL behavior in these disordered systems, there is mounting experimental evidence that disorder should not be neglected in any eventual model of NFL behavior in these materials. Precisely what role disorder plays remains to be established unambiguously. It is clear, however, from a number of studies that NFL effects can be found in disordered materials that are relatively far from a $T = 0$ boundary by virtually any measure of nearness to this boundary. An interesting case is $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$ in which $C_m/T \propto -\ln T$ even for $x = 1.4$. [23] This would suggest that disorder may be more important than proximity to a quantum critical point for producing NFL behavior in these materials.

5. Summary

The contrasting behaviors of CeRh_2Si_2 and $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$ near their respective $T = 0$ magnetic-non-magnetic boundary are striking. Even when measurements are performed relatively near the critical point in CeRh_2Si_2 ($P/P_c = 0.97$ and 1.09), there is no clear evidence for NFL behavior that might be expected from quantum-critical fluctuations. Extending these thermodynamic measurements to lower temperatures and to pressures yet closer to P_c should help clarify conditions under which NFL effects appear in well-ordered compounds. On the other hand, chemical and attendant hybridization disorder in $\text{CeRh}_{2-x}\text{Ru}_x\text{Si}_2$ produces NFL-like behavior even relatively far from a quantum-phase transition. Pressure studies on well-characterized, preferably single-crystal, samples will be necessary to understand the relationship between NFL features and the appearance of superconductivity near a $T = 0$ magnetic-non-magnetic boundary in isostructural CeM_2X_2 compounds.

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