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Response of CeRh_2Si_2 to Pressure

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Abstract: Under atmospheric pressure, CeRh_2Si_2 orders antiferromagnetically at $T_N=35$ K, with magnetic entropy $S=R\ln 2$ associated with the ordered groundstate. Application of modest pressure (≈ 9 kbar) to CeRh_2Si_2 suppresses T_N to near zero Kelvin, increases its Sommerfeld coefficient of specific heat by nearly a factor of 3.5 and induces some form of superconductivity below 400 mK that is depressed by a magnetic field at a rate of -80 mK/kG.

keywords: CeRh_2Si_2 , pressure, specific heat, superconductivity

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1. Introduction

Cerium, Yb and U compounds forming in the ThCr_2Si_2 structure exhibit a broad range of Kondo-lattice phenomena, including superconductivity, long range magnetic order, coexisting superconductivity and magnetism and paramagnetism. A common view is that this variety in groundstates arises from the competition between coexisting Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, with the balance being set by the magnitude of the d-f exchange J that is proportional to the square of the d-f hybridization matrix element V divided by the energy difference ΔE of the f-level from the Fermi energy. [1] For small J , localized f-moment magnetism is favored and at larger J Kondo-spin compensation favors a paramagnetic state in which electronic correlations are important. [2] Superconductivity is believed to appear near the magnetic-non-magnetic boundary. [1] The extent to which this simple view captures all the important physics remains to be tested, but it has been used to interpret qualitatively the systematic variation in groundstates in CeM_2Si_2 [3,4], CeM_2Ge_2 [5] and U-based analogues [6] with changes in applied pressure, transition-metal-M or effect of "chemical pressure" produced by substituting smaller Si for larger Ge.

The CeM_2Si_2 series has received considerable attention, primarily because of heavy-fermion superconductivity in CeCu_2Si_2 but also because all of the above mentioned groundstates exist in this series. In Ce-based correlated electron systems, there is substantial evidence that J increases with decreasing volume. [1] Consequently, in the absence of direct measures of J , systematics in the groundstate are frequently discussed in terms of the unit cell volumes at ambient pressure [4-6] or the pressure dependence [3] of the Neel temperature T_N in this series. Two members, $M=\text{Pd}$ and Rh , show a rapid decrease in T_N with applied pressure [3], suggesting that both may be near the magnetic-non-magnetic boundary and that there is the possibility of pressure-induced superconductivity.

Jaccard et al. [7] have taken a different but related approach to the systematic of this series. They noted a variation in the low-temperature thermoelectric power as a function of a corrected unit cell volume that suggested the possibility of inducing superconductivity in CeCu_2Ge_2 with sufficiently high applied pressure. Indeed, they found that pressure decreases $T_N(P=0) \approx 4.0$ K to near zero for $P \geq 75$ kbar, and that at and above this pressure superconductivity develops below $T_c \approx 650$ mK. (Careful low pressure measurements [8] show that T_N initially increases weakly with pressure before decreasing rapidly, precisely as expected from competing Kondo and RKKY interactions.) For $P \approx P_c$, the resistivity increases just above T_c as AT^2 , with $A \approx 10 \mu\Omega\text{cm}/\text{K}^2$ at $P=101$ kbar. This large T^2 -coefficient of resistivity and large upper critical field ($B_{c2}(T=0, P=101 \text{ kbar}) \approx 2$ T) are consistent with superconductivity in a strongly correlated Fermi liquid. The thermopower-based analysis of Jaccard et al. [7], however, would probably not suggest pressure-induced superconductivity in CeRh_2Si_2 but possibly would suggest it for CePd_2Si_2 . To test predictions from these two approaches to the systematics of CeM_2Si_2 compounds, we have

performed high pressure resistance and ac susceptibility measurements on CeRh_2Si_2 . The specific heat of CeRh_2Si_2 was determined at ambient and high pressures to help interpret our observations.

2. Experimental

Several nominally stoichiometric CeRh_2Si_2 and off-stoichiometry ($\text{Ce}_{0.97}\text{Rh}_2\text{Si}_2$, $\text{CeRh}_{2.2}\text{Si}_2$ and $\text{CeRh}_{1.5}\text{Si}$) samples were prepared by arc melting. Except for the $\text{CeRh}_{1.5}\text{Si}$ sample, the dominant phase in each formed in the ThCr_2Si_2 structure. Small bars were cut from the melted buttons for resistance and ac susceptibility measurements in a self-clamping pressure cell which used Flourinert as the pressure transmitting medium. A small piece of lead served as the pressure manometer. Specific heat measurements at ambient pressure were performed from 0.4 to 45 K using an adiabatic technique on a 2.549- gm piece of nominally stoichiometric material. High pressure specific heat was measured from 0.4 to 19 K in a Be-Cu cell on a 2.847 gm cast-rod, also of nominally CeRh_2Si_2 ; AgCl acted as the pressure medium. However, on this sample, a very small specific heat peak appeared near 5 K that was due to antiferromagnetic ordering in about 0.0028 moles of CeRh_3Si_2 . This contribution was subtracted in further data analysis. Details of the specific heat measurements will be published elsewhere. [9]

3. Results and Discussion

Figure 1 shows that magnetic specific heat $C_m(T) = C_{\text{CeRh}_2\text{Si}_2}(T) - C_{\text{LaRh}_2\text{Si}_2}(T)$ divided by temperature and corresponding magnetic entropy of $S(T)$ of CeRh_2Si_2 . The peak in C_m/T at 35 K signals the onset of antiferromagnetic order, as found in magnetic susceptibility and resistivity measurements. The entropy reaches almost full $R\ln 2$ at T_N , consistent with magnetic ordering in a doublet groundstate. Quasielastic neutron scattering [4] gives a spin-fluctuation (Kondo) temperature $T_K = 33$ K just above T_N that decreases rapidly below T_N . Consequently, most of the magnetic entropy should be associated with ordering of the 4f moments. In the absence of ordering, the specific heat Sommerfeld coefficient can be estimated from $\gamma = (N-1)\pi R/6T_K$, where N is the groundstate degeneracy ($N=2$ in this case) and R is the gas constant. From this single Kondo-impurity relationship, we calculate $\gamma = 130$ mJ/mole K^2 . The observed T-linear contribution to C_m at low temperatures is 22.8 mJ/mole K^2 . This large reduction of γ in the ordered state is found commonly in Ce-based magnets and may be attributed to the existence of a large internal magnetic field produced by the 4f-moment ordering that quenches, at least partially, Kondo-like spin fluctuations. [10]

The temperature-dependent resistivity $\rho(T)$ of CeRh_2Si_2 at various pressures is plotted in Fig. 2(a): At ambient pressure, the Neel temperature is indicated clearly by a sharp drop; whereas, $\partial\rho/\partial T$ closely resembles C_m/T , with a well-defined peak at 35 K. With increasing pressure, T_N moves rapidly to lower temperatures; at $P=12.4$ kbar, there is no obvious evidence for a magnetic transition and $\partial\rho/\partial T$ passes through a broad maximum centered near 30 K. The maximum value of $\partial\rho/\partial T$ is over a factor of three smaller than its peak value at ambient pressure. Further increasing pressure shifts the broad maximum in $\partial\rho/\partial T$ to higher temperatures and reduces its magnitude. Fig. 2(b) shows the effect of pressure on $\rho(T)$ below 30 K. At ambient and 7.3 kbar

pressures, $\rho(T)$ increases approximately as T^3 , but once antiferromagnet order is suppressed, a Fermi-liquid T^2 -dependence develops over a low-temperature interval that increases with pressure and with a slope that decreases correspondingly.

The pressure dependence of T_N , plotted in Fig. 3(a), compares favorably to that determined earlier [3] and shows that $T_N \rightarrow 0$ at a critical pressure $P_c = 9 \pm 1$ kbar. The magnetic specific heat divided by T at 7.1 kbar and at temperatures to 19 K has a temperature dependence similar to data obtained at lower pressures. At 11.0 kbar and higher pressures, the temperature dependence of C_m/T changes and there is no evidence for a magnetic transition above 0.4 K. Together these data are consistent with the phase diagram in Fig. 3 (a). Interestingly, $\gamma(P)$ increases smoothly from $P=0$ and passes through a broad maximum near 14 kbar with a magnitude of 80 mJ/mole K^2 . The pressure at which γ is a maximum is 5 to 6 kbar greater than the pressure necessary to suppress T_N toward zero. This suggests that, although long range order does not exist in this pressure range, relatively significant antiferromagnetic correlations must remain. From the maximum value of γ and the single impurity relationship given in Sec. 1, we estimate $T_K = 54$ K at 14 kbar, which is 21 K higher than the $P=0$ value found from quasi-elastic neutron scattering. This change in T_K gives $\partial T_K / \partial P \approx 1.5$ K/kbar, which is comparable to $\partial T_K / \partial P = 0.8$ K/kbar deduced [11] for the isostructural heavy-fermion superconductor $CeCu_2Si_2$.

To look for superconductivity in $CeRh_2Si_2$, resistance and ac susceptibility measurements were made on several samples at temperatures to 50 mK. None of the samples of various stoichiometries, including $CeRh_3Si_2$, exhibited superconductivity at ambient pressure. However, as shown in Fig. 4, some samples do show a superconducting transition near 400 mK at elevated pressures. These transitions appear only in normally stoichiometric $CeRh_2Si_2$, and even in one of these, the resistive transition was not complete. High pressure experiments on $CeRh_3Si_2$ confirmed that this material is not superconducting above 50 mK, and, therefore, even if present as a trace second phase, it could not be responsible for the results shown in Fig. 4. The effect of a magnetic field on T_c (defined from the onset of superconductivity) is given in the inset of Fig. 4 for a $CeRh_2Si_2$ sample at 11.0 ± 0.5 kbar. Extrapolating these data to zero Kelvin gives an upper critical field $B_{c2}(0) = 0.35$ T, a value about one-half the Pauli paramagnetic limiting field for a BCS superconductor with $T_c = 350$ mK. From $B_{c2}(0)$, we estimate the coherence length $\xi_o = \sqrt{\Phi_o / 2\pi B_{c2}(0)} \approx 94$ Å. The slope B'_{c2} near T_c is -1.3 T/K, and thus the $T=0$ orbital critical field is estimated to range from 0.33 to 0.31 T assuming clean and dirty limit relationships, respectively.

The questions remain whether this superconductivity is intrinsic to $CeRh_2Si_2$ and, if it is, whether it should be considered "heavy-fermion" superconductivity. It is known [12] that the stoichiometric range of $LaRh_2Si_2$ is extremely narrow and that slight ($\sim 1\%$) changes in nominal composition produce eight ternary compounds, several of which are superconducting. Our observation that pressure-induced superconductivity is absent in off-stoichiometric samples argues

strongly against superconductivity in secondary phases. We speculate that the lack of a complete resistive transition in one nominally stoichiometric sample may be due, in fact, to some very slight off-stoichiometry in that case. Further, as shown in Fig. 3(b), superconductivity appears only for pressures near the critical pressure required to suppress antiferromagnetic order and this suggests that it develops out of the electronically correlated state intrinsic to CeRh_2Si_2 . The relationship between $T_N(P)$ and $T_c(P)$ given in Figs. 3(a) and (b) is very similar, albeit at a different pressure scale, to that found [7] in CeCu_2Ge_2 and very recently [13] in CePd_2Si_2 , where $P_c \geq 25$ kbar, and suggests that this behavior could be a rather common feature of Ce-based ThCr_2Si_2 -type magnets. We will return to this point.

Concerning the question of whether CeRh_2Si_2 might be considered a heavy-fermion superconductor, it is worth comparing our observations to other superconductors. UPt_3 has a similar T_c and $\rho(T \geq T_c)$ but a γ that is six times larger. [14] From the relationship $B'_{c2} \propto \gamma \rho$, the differences in γ values account largely for the differences in B'_{c2} (-4 to -6 T/K for UPt_3 versus -1.3 T/K for CeRh_2Si_2). URu_2Si_2 has a γ comparable to CeRh_2Si_2 at 9 kbar but a resistivity near T_c that is about a factor of ten larger. [14] Again from the expression for B'_{c2} , the differences in $\rho(T \geq T_c)$ account largely for differences in B'_{c2} (-7.6 T/K for URu_2Si_2). However, relative to CeCu_2Si_2 ($\gamma \approx 1000$ mJ/mole K^2 , $\rho(T \geq T_c) = 65 \mu\Omega\text{cm}$ and $B'_{c2} = -10 - 23$ T/K), B'_{c2} for CeRh_2Si_2 is much larger, using the same sort of comparison. In contrast, LaRh_2Si_2 is a type-I superconductor with $T_c = 74$ mK and $B_c(0) = 0.73$ mT. [12] From this cursory comparison, it appears that superconductivity in CeRh_2Si_2 , if it is intrinsic, may be similar to that in acknowledged heavy-fermion superconductors.

Finally, we return briefly to systematics among CeM_2Si_2 compounds. Table I lists properties of several of these. As mentioned in Sec. 1, the variation of T_N among these materials is qualitatively consistent with expectations for a volume-dependent competition between Kondo and RKKY interactions. There are, however, many unanswered questions related to this view. For example, why is T_N so high for CeRh_2Si_2 ? Why is T_N low for CeCu_2Ge_2 relative to CePd_2Si_2 and CeAg_2Si_2 ? Why is there no phase transition in CeRu_2Si_2 ? In spite of these and other questions, there is, however, a qualitative correlation with ambient pressure unit-cell volume and the critical pressure P_c required to induced superconductivity. This is summarized in the last two columns in Table where we compare the critical pressure P_c and the difference in ambient pressure unit-cell volume relative to that of CeCu_2Si_2 . Assuming a bulk modulus of 1 Mbar for all of the compounds, the relative volume differences correspond to a "chemical" pressure (in kbar) of 10 times the % difference, i.e. $1.4\% > 14$ kbar. To within roughly a factor of two the estimated chemical pressure agrees with the observed P_c . If this observation is more than a coincidence, it suggests the possibility of pressure-induced superconductivity in other members of this series.

4. Summary

Pressure studies of stoichiometric CeRh_2Si_2 find a rapid suppression of antiferromagnetic order with decreasing volume that terminates in a superconducting phase above about 9 kbar with

$T_c \approx 400$ mK. Both specific heat and resistivity measurements indicate that superconductivity develops within a modestly correlated Fermi-liquid. Additional experiments are required to confirm that this superconductivity is bulk and, if so, precisely under what material conditions it develops. Inspection of the variation of CeM_2X_2 properties with cell volume suggests that pressure-induced superconductivity in $CeRh_2Si_2$ may be similar to that found in other members of the series and that other members may be candidates for exhibiting pressure-induced superconductivity.

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Table 1: Properties of CeM_2X_2 compounds

<u>Material</u>	<u>$T_0(\text{K})^{(a)}$</u>	<u>$V(\text{\AA}^3)^{(b)}$</u>	<u>$P_c(\text{kbar})^{(c)}$</u>	<u>$(V-V_{\text{Cu}})/V_{\text{Cu}}\%^{(d)}$</u>
CeCu_2Si_2	0.640	167.4	0	0
CeRh_2Si_2	35	169.8		1.4
	0.40		9 ± 1	
CeRu_2Si_2	--	171.9	--	2.7
CePd_2Si_2	10.0	177.0		5.7
	0.50		$27\pm 2^{(e)}$	
CeCu_2Ge_2	4.1	177.7		6.2
	0.60		$77\pm 2^{(f)}$	
CeAg_2Si_2	9.7	184.7		10.3
CeAu_2Si_2	10.2	191.6		14.4

(a) Values greater than 1 K correspond to T_N ; values less than 1 K are superconducting transition temperatures.

(b) Unit cell volume from Ref. 15.

(c) Critical pressure required to induce superconductivity.

(d) Unit cell volumes compared to that of CeCu_2Si_2 (V_{Cu}).

(e) Ref.13.

(f) Ref. 7.

Figure Captions:

- Fig. 1. Magnetic specific heat C_m divided by temperature versus temperature. C_m was determined by subtracting the specific heat of LaRh_2Si_2 from that of CeRh_2Si_2 . Solid curve is the magnetic entropy S as a function of temperature. The dotted line corresponds to $S=R\ln 2$.
- Fig. 2 (a) Electrical resistivity ρ versus temperature for CeRh_2Si_2 at various applied pressures. (b) Expanded view of the low temperature variation of $\rho(T)$. At 12.4 kbar, $\rho(T) \propto AT^2$ with $A=0.0076 \mu\Omega\text{cm}/\text{K}^2$, and at 17 kbar, $A=0.0047 \mu\Omega\text{cm}/\text{K}^2$.
- Fig. 3 (a) Neel temperature $T_N(P)$ normalized by its value at ambient pressure ($T_N(0)=35\text{K}$) as a function of pressure. Open circles are from Ref. 3; open diamonds are present work; dashed line is a guide to the eye. (b) Onset superconducting transition temperature T_c versus pressure. Solid circles correspond to measurements on a sample that showed an incomplete resistive transition; solid triangles are from a sample that showed a complete, within experimental resolution, resistive transition to a superconducting state.
- Fig. 4 Resistivity ρ , left ordinate, and ac susceptibility χ_{ac} , right ordinate, as a function of temperature for two different CeRh_2Si_2 samples. Resistivity data were obtained at $P=11$ kbar and χ_{ac} at $P=9.5$ kbar. The inset shows the effect of magnetic field on the superconducting transition temperature of the resistivity sample.

Fig. 1

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Fig. 2(a)

Yl-t, org

Fig. 2(b)