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Superconductivity in heavy-fermion $CeRh_2Si_2$

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We report the discovery of a superconducting transition in the heavy-fermion compound $CeRh_2Si_2$ under hydrostatic pressure. Superconductivity appears at pressures above about 9 kbar, near the critical pressure required to suppress antiferromagnetic order $[T_N(P=0)=36\ \mathrm{K}]$. Onset of superconductivity occurs at a temperature of ≈ 350 mK. Resistivity measurements as a function of field at constant temperature allow us to build an H^*-T phase diagram for the onset of superconductivity. A Ginzburg-Landau analysis of the initial slope of the critical field leads to an effective mass of $m^*/m_0 \approx 200$, supporting the heavy-fermion nature of superconductivity in $CeRh_2Si_2$. Magnetic ac susceptibility (χ_{ac}) shows a diamagnetic response corresponding to about 1% of perfect diamagnetism. The size of the feature in χ_{ac} also is strongly peaked at a pressure of ≈ 9 kbar.

INTRODUCTION

Unconventional superconductivity is a very active area of research, both in cuprate and heavy-fermion compounds. These two classes of materials hold the possibility that the attractive interaction between charge carriers originates not from electron-phonon interaction, as in conventional superconductors, but rather from the magnetic fluctuations present in these systems. In heavy-fermion compounds these fluctuations are thought to arise primarily from Kondo coupling of partially filled $4f$ (for Ce) or $5f$ (for U) shells to conduction electrons.

The first discovery of heavy-fermion superconductivity was in $CeCu_2Si_2$ (Ref. 1) with a transition temperature $T_c \simeq 0.5$ K at zero pressure. By measuring the magnitude of the heat capacity jump at T_c, the authors demonstrated convincingly that the phase transition developed out of a band of heavy quasiparticles. Subsequently, superconductivity has been discovered in a small number of U-based heavy-fermion compounds, namely, UPt_3,[2] UBe_{13},[3] URu_2Si_2,[4] UNi_2Al_3,[5] UPd_2Al_3.[6] In some of these compounds, superconductivity coexists with a magnetically ordered state, with Néel temperature T_N about an order of magnitude higher than T_c.

Until recently, $CeCu_2Si_2$ represented the only example of a Ce-based heavy-fermion superconductor. However, Jaccard *et al.*[7] have discovered that isostructural $CeCu_2Ge_2$ also superconducts below $T_c \simeq 0.6$ K at pressures above 70 kbar. Investigation of this compound was prompted by the systematic variation of the thermopower of compounds of the CeM_2X_2 series as a function of the unit-cell volume. At low temperatures $CeCu_2Ge_2$ has negative thermopower, as does superconducting $CeCu_2Si_2$, and a unit-cell volume slightly larger than that for $CeCu_2Si_2$. Applying hydrostatic pressure was expected (and observed) to further decrease the thermopower along a smooth curve passing through the data points for the CeM_2X_2 series towards $CeCu_2Si_2$. At the same time, the Néel temperature of $CeCu_2Ge_2$ was suppressed by hydrostatic pressure from $T_N=4.1$ K at ambient pressure to zero, near the pressure at which the superconducting ground state appeared. Very recently another antiferromagnetic member of the CeM_2X_2 series (where M stands for transition metal, and X is either Si or Ge), $CePd_2Si_2$, was also found to undergo a superconducting transition below $T_c \simeq 500$ mK upon application of hydrostatic pressure of more than 25 kbar.[8] This transition was identified as a drop in resistance of the sample below the detection limit. It is not obvious from existing data[7] that the same systematics of thermopower apply to $CePd_2Si_2$, and certainly not to $CeRh_2Si_2$, whose ambient pressure thermopower and cell volume would indicate that it should not become superconducting at smaller cell volume. In our investigation of $CeRh_2Si_2$, also a member of the CeM_2X_2 series of compounds, we establish other systematic variations in the properties of these materials that may be a more reliable prognosticators of superconductivity.

The electrical resistivity of $CeRh_2Si_2$ as a function of hydrostatic pressure was studied earlier[9] in a temperature range above 1.2 K as a part of an investigation of Néel transitions in the CeM_2Si_2 series, with M = Ag, Au, Pd, and Rh. The T-P phase diagram for $CeRh_2Si_2$ obtained[9] indicated a strong nonlinear decrease in T_N as a function of hydrostatic pressure, which suppresses the magnetic order below detectable limits at a pressure of about 8.5 kbar. This raises the possibility of recovering a superconducting ground state which maybe suppressed by magnetic order at lower pressures.

EXPERIMENTAL RESULTS

$CeRh_2Si_2$, as most other members of CeM_2X_2 series, forms in the $ThCr_2Si_2$ body-centered tetragonal structure. The samples were prepared by arc-melting stoichiometric quantities of the elements on a water-cooled Cu hearth in an argon atmosphere. All of the elements were melted together during the first melt. The samples were melted and turned more than 10 times, removed from the melter, and crushed, and then remelted and turned at least 10 more times. The samples were about 20 g in mass. A vacuum was pumped quickly on the large buttons after the last melt to promote slow cooling, in lieu of a post-melting anneal. Pieces for

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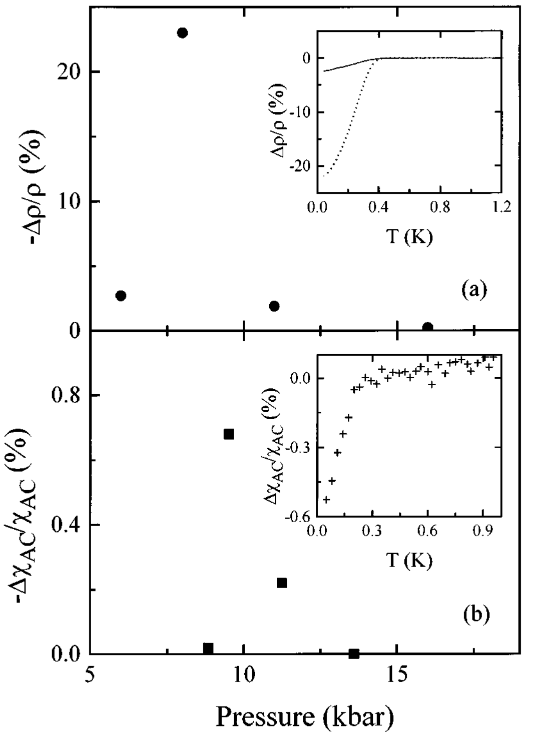

FIG. 1. (a) Relative resistivity decrease of one $\mathrm{CeRh_2Si_2}$ sample as function of pressure; peak is at $P=8$ kbar. Inset, resistivity normalized to its value above the transition; solid line, 6 kbar, dotted line, 8 kbar. (b) Relative susceptibility drop for another $\mathrm{CeRh_2Si_2}$ sample as a function of pressure; maximum value is for $P=9.5$ kbar. Inset, relative susceptibility change as a function of temperature at a pressure of $P=9.5$ kbar.

measurements were cut from the center of the button. Powder x-ray diffraction showed no other crystallographic phases. Both resistivity and ac magnetic susceptibility measurements were performed in a self-clamping Be-Cu pressure cell,[10] with fluorinert as a pressure-transmitting medium. A superconducting lead manometer was used to measure hydrostatic pressure in the cell.

The inset of Fig. 1(a) shows results of resistivity measurements as a function of temperature between 50 mK and 1.2 K on the first sample of $\mathrm{CeRh_2Si_2}$. The two curves correspond to pressures of 8 ± 0.5 and 11 ± 0.5 kbar. This particular sample did not become completely superconducting at any of the four pressures studied. The pressure dependence of the maximum suppression of resistivity, shown in the main part of Fig. 1(a) as a function of pressure, is, however, instructive in that it shows a strong peak in the tendency toward superconductivity at a pressure of ≈ 8 kbar, a value near the critical pressure required to suppress antiferromagnetic order in this compound.

Figure 1(b) displays results of ac magnetic susceptibility χ_{ac} measurements on another nominally stoichiometric sample of $\mathrm{CeRh_2Si_2}$. The inset shows the magnetic response to a temperature sweep at a pressure of 9.5 kbar. The magnitude of the "diamagnetic" feature in χ_{ac} is less than 1%, estimated by comparing it to the magnitude of a signal from a similar-size piece of lead. The pressure dependence of the magnitude of the suppression of the χ_{ac} signal is shown in the main part of Fig. 1(b). Similarity in the pressure dependence of χ_{ac} and ρ, in particular the peaking of the relative change at 9 ± 1 kbar, indicates that features in both χ_{ac} and ρ are due to the same phase transition, namely, superconductivity.

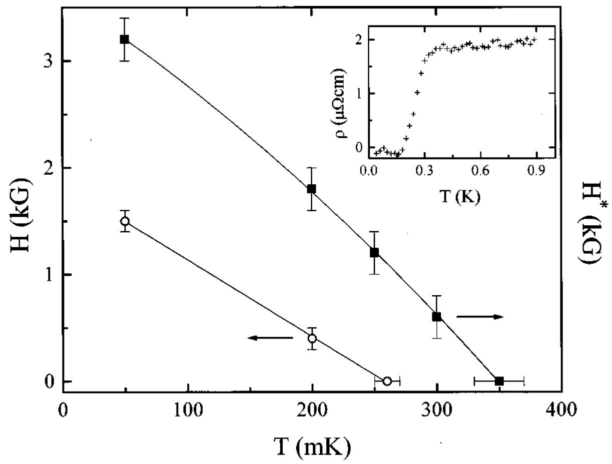

FIG. 2. Magnetic field at the onset of suppression of resistivity (H^*, solid squares; solid line is a guide to the eye) and the midpoint of the transition (H, ○) as a function of temperature at a pressure of 11.0 ± 0.3 kbar. Error bars represent systematic uncertainty in our method of determining the onset and midpoints of the superconducting transitions. Inset, superconducting transition displayed in resistivity data at 11.0 ± 0.3 kbar.

Figure 2 gives resistivity data on a third $\mathrm{CeRh_2Si_2}$ sample at a pressure of 11.0 ± 0.3 kbar. The inset shows data for a temperature sweep in zero magnetic field. The resistivity drops to zero within instrumental resolution around 200 mK, whereas the onset of the drop in resistivity occurs at 350 mK, with the midpoint at $T=260$ mK. In the main part of Fig. 2 we plot the magnetic-field–temperature phase diagram for $\mathrm{CeRh_2Si_2}$ at 11 kbar. Solid squares indicate the onset of the resistance decrease (H^*, T) points, whereas open circles give (H,T) coordinates of the midpoint of the transition. The slope of the H^* vs T data near T_c, $\delta H^*/\delta T$, together with values of Sommerfeld coefficient γ, T_c, and resistivity ρ_0 above T_c, allows us to estimate superconducting and normal state properties within the framework of Ginzburg-Landau theory, as has been done for A 15 superconductors[11] as well as $\mathrm{CeCu_2Si_2}$.[12] As input parameters we use H^* data ($H'_{c2}=\delta H^*/\delta T=-14$ kG/K) and measured values of $\gamma=80$ mJ/mol K^2,[13] $T_c=0.35$ K, and resistivity $\rho_0=2$ $\mu\Omega$ cm. $\mathrm{CeRh_2Si_2}$ at 11 kbar appears to be close to the clean limit, with the "dirty limit" term accounting for roughly 10% of H'_{c2}. Au analysis following that done for $\mathrm{CeCu_2Si_2}$ (Ref. 13) provides estimates for the superconducting part of the Fermi surface, $S_s=3.1\times10^{20}$ m^{-2}, BCS coherence length $\xi_0=370$ Å, total elastic mean free path $\ell_{\mathrm{tr}}=2300$ Å, and Fermi velocity $v_F=9.5\times10^3$ m/s; these can be compared to $S_s=13\times10^{20}$ m^{-2}, $\xi_0=89$ Å, $\ell_{\mathrm{tr}}\geqslant 20$ Å, and $v_F=4.5\times10^3$ m/s for $\mathrm{CeCu_2Si_2}$.[12] Using the room-temperature resistivity to estimate the Fermi momentum, along the argument of Ref. 12, we obtain $k_F=1.8\times10^{10}$ m^{-1} and from the ratio k_F/v_F an estimate of the effective mass $m^*/m_0\approx220$ [$k_F=1.5\times10^{10}$ m^{-1} and $m^*/m_0=380$

for $CeCu_2Si_2$ (Ref. 12)]. A variation on the expression for the effective mass given in Ref. 12 (valid in a clean limit),

$$m^*/m_0 = \sqrt{\frac{H'_{c2}}{T_c}} k_F ,$$

shows that the large effective mass is a consequence of a low-T_c and a steep H^*-T phase boundary near T_c.[14] Taking the slope of the midpoint of the transition with respect to magnetic field instead of $\delta H^*/\delta T$ (see Fig. 2) results in an effective mass ratio smaller by $\approx 30\%$. Likewise, taking the value of the Fermi momentum for isostructural $CeCu_2Si_2$, instead of the estimate from the room-temperature resistivity obtained above, would result in lowering of the effective mass estimate by $\approx 20\%$. A factor of 2–3 difference in m^* between $CeCu_2Si_2$ and $CeRh_2Si_2$, in spite of the order of magnitude difference in γ [for $CeCu_2Si_2$ $\gamma = 0.7$ J/K^2 mol (Ref. 12)], suggests that heavy quasiparticles may be created on similar parts of the Fermi surface in the two compounds, but the fraction of the Fermi surface that is involved in that process is much smaller for $CeRh_2Si_2$. The value $m^*/m_0 \approx 200$ obtained from this Ginzburg-Landau analysis supports the heavy-fermion nature of superconductivity in $CeRh_2Si_2$.

Because both complete and incomplete superconducting transitions were observed in nominally stoichiometric $CeRh_2Si_2$ samples, we also have prepared several off-stoichiometric samples, including $Ce_{0.97}Rh_2Si_2$ and $CeRh_{2.2}Si_2$, as well as $CeRh_3Si_2$, which was identified as a trace impurity phase in heat-capacity measurements on $CeRh_2Si_2$.[13] None of these samples show any sign of superconductivity in the pressure range where superconductivity in nominally stoichiometric samples was observed. This leads us to conclude that superconductivity is associated with stoichiometric $CeRh_2Si_2$. In fact, different behaviors of nominally stoichiometric compounds indicate extreme sensitivity to composition, where slight deviation from exact stoichiometry leads to suppression of superconductivity. This behavior is reminiscent of that found in early studies of $CeCu_2Si_2$.[1] We have recently learned that an attempt has been made to repeat the measurements on $CePd_2Si_2$,[15] and superconductivity was not observed. Whether important criteria for good superconducting samples are precise stoichiometry, low residual resistivity, or perhaps some other property is an important question posed by our (and others') recent results, an answer to which may shed light on the mechanism of the superconductivity in these materials.

DISCUSSION

Figure 3 shows the resulting P-T phase diagram for $CeRh_2Si_2$. The superconducting phase appears in the vicinity of where hydrostatic pressure suppresses magnetic order below detectable limits. This is a common feature of pressure-induced superconductivity in $CeCu_2Ge_2$ and $CePd_2Si_2$, both of which order magnetically at ambient pressure. The question remains whether magnetism and superconductivity coexist in the same crystallographic phase, which appears not to be the case in $CeCu_2Si_2$.[16] An important criterion for the observation of superconductivity in CeM_2X_2 compounds appears to be their proximity to magnetism, which suggests that spin fluctuations may be important for pairing. Further investigations of other members of the CeM_2X_2 series may clarify this question.

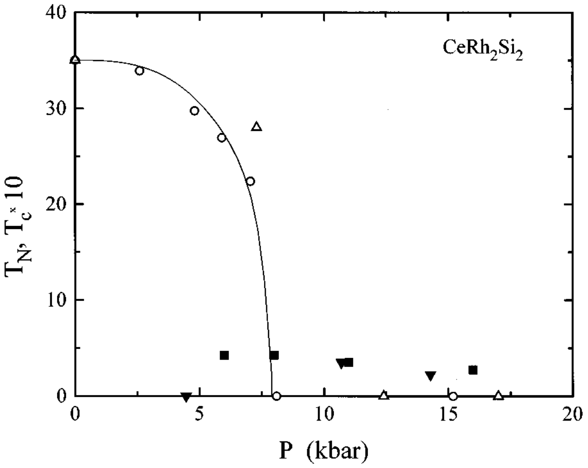

FIG. 3. P-T phase diagram of $CeRh_2Si_2$. Open symbols represent the aniferromagnetic ordering transition $T_N(P)$. Solid symbols are $T_c(P)$ points of the superconducting transitions obtained from the onset of suppression of resistivity for several samples that are represented by different symbols. The error bars are on the order of the size of the symbols and therefore omitted. Notice the different temperature scales for the two phase transitions.

It appears now that three members of CeM_2X_2 series undergo a superconducting phase transition once antiferromagnetic order is suppressed by the application of hydrostatic pressure. There exists a qualitative correlation between the unit-cell volume of these compounds (Table I) and the pressure necessary to drive them superconducting: The larger the cell volume, the greater the required pressure. This suggests that there is a favorable cell volume of 168±4 Å^3 in this series at which superconductivity chooses to appear. One would then expect other members of the series to become superconducting at pressures on the order of a few hundred kbar.

SUMMARY

We have observed a reduction of resistivity (both complete and incomplete) and diamagnetic response of χ_{ac} in $CeRh_2Si_2$ under hydrostatic pressure. Based on the pressure dependence of the magnitude of these effects, we conclude that they represent signatures of the same phenomenon, that

TABLE I. Properties of superconducting CeM_2X_2 compounds.

Material	T_c (K)	V (Å^3)[a]	P_c^{obs} (kbar)[b]	V_c^{calc} (Å^3)[c]
$CeCu_2Si_2$	0.64	167.4	0	167.4
$CeRh_2Si_2$	0.35	169.8	9±1	168.3
$CePd_2Si_2$	0.50	177.0	27±2 (Ref. 8)	172.2
$CeCu_2Ge_2$	0.60	177.7	77±2 (Ref. 7)	164.0

[a] Ambient pressure unit-cell volume from Ref. 17.

[b] Critical pressure required to induce superconductivity.

[c] Unit-cell volume at the critical pressure, assuming a bulk modulus of 1 Mbar.

of a superconducting phase transition. Several similarities are drawn among $CeRh_2Si_2$ and other superconducting compounds of the CeM_2X_2 series. It appears that in these compounds the antiferromagnetic order must be suppressed at least partially if not completely before superconductivity is observed. It remains to be answered whether $CeRh_2Si_2$ is like most of the U-based heavy-fermion superconductors, in which superconductivity and magnetic order coexist. The superconductivity in $CeRh_2Si_2$ is very sensitive to precise composition. We believe that the stoichiometric phase is responsible for superconductivity, and slight deviations from it result in suppression of the superconducting state. Further work is required to clarify these questions.

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[14] It is also possible to estimate k_F from the free-electron expression for the bulk modulus, which we assume to be equal to 1 Mbar, a value common to CeM_2X_2 compounds. In this case we obtain $k_F = 1.5 \times 10^{10}\ \mathrm{m}^{-1}$ and $m^*/m_0 = 170$.

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