PHYSICAL REVIEW B VOLUME 30, NUMBER 1 1 JULY 1984

Superconductivity in a mixed-valent system: $CeRu_3Si_2$

U. Rauchschwalbe, W. Lieke, and F. Steglich
Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

C. Godart,* L. C. Gupta,† and R. D. Parks
Department of Physics, Polytechnic Institute of New York, Brooklyn, New York 11201

(Received 5 March 1984; revised manuscript received 21 May 1984)

Low-temperature properties characterize the hexagonal compound $CeRu_3Si_2$ as a mixed-valent system intermediate between weakly mixed-valent systems like $CeSn_3$ or $CePd_3$ and strongly mixed-valent systems like $CeRu_2$. The dimensionless ratio of the Pauli susceptibility ($\chi_0 \simeq 9.4\times10^{-4}$ emu/mole) and the linear specific-heat coefficient ($\gamma \simeq 39$ mJ/mole K^2) is about 0.8. $CeRu_3Si_2$ exhibits type-II superconductivity below $T_c \simeq 1$ K, which is much lower than $T_c \simeq 7$ K of the La homolog.

It has been believed for a long time that the occurrence of superconductivity in Ce intermetallic compounds necessarily requires a nonmagnetic, i.e., tetravalent ($4f^0$), configuration of the Ce ions. Therefore, the superconducting compounds $CeRu_2$ ($T_c \simeq 6$ K)[1] and $CeCo_2$ ($T_c \simeq 1$ K)[2] as well as the high-pressure α' phase of metallic Ce ($T_c \leq 1.9$ K)[3] have been considered tetravalent Ce systems. Recent thermodynamic considerations,[4] $2p$ x-ray absorption edge,[5] and resonant x-ray photoemission[6] measurements, however, strongly suggest substantial $4f$ occupation in the above two intermetallics. It is, therefore, now widely contended that both $CeRu_2$ and $CeCo_2$, and perhaps also α'-Ce, belong to the class of so-called "strongly mixed-valent" materials.[7] This means that there exists strong $4f$ hybridization with the conduction-band states resulting in a band of hybridized one-particle states at the Fermi level E_F with typical width $\Delta \sim 0.1$ eV.[7] In the weakly mixed-valence (MV) materials like $CeSn_3$, $CePd_3$, $CeBe_{13}$, etc, Δ is smaller, i.e., a few 0.01 eV.[7] So far, none of these weakly MV systems was found to superconduct. This is especially interesting in view of the discovery of "heavy-fermion" superconductivity below $T_c \approx 0.6$ K in $CeCu_2Si_2$,[8] which has to be classified among the nearly trivalent or Kondo-lattice systems.[9] The heavy-fermion properties of such a material at low temperature originate in the existence of a very narrow (many-body) resonance of width < 1 meV at the Fermi level. Very recently, the actinide compound UBe_{13} was found[10] to show the same exotic low-temperature behavior as $CeCu_2Si_2$.

The present study was motivated by the search for further Ce-based MV superconductors. We discuss here the results of lattice parameter, resistivity, susceptibility, and specific-heat measurements on the hexagonal compound $CeRu_3Si_2$. Its La, Y, and Th homologs have recently been reported[11] to become superconducting, with $LaRu_3Si_2$ showing the highest T_c of 7 K. It was reported in Ref. 12 that the structure of these compounds, which belongs either to the space group $P6_3/m$ or $P6_3$, can be obtained by weighing in some excess of Ru, which exists as free Ru in the molten ingot.

Two polycrystalline samples of $CeRu_3Si_2$ were prepared in an argon arc furnace by melting together the weighted constituents with nominal composition $CeRu_{3.5}Si_2$ (sample no. 1) and $CeRu_{3.3}Si_2$ (sample no. 2). According to the x-ray powder diffraction patterns taken at room temperature, the samples consist of $CeRu_3Si_2$ and some precipitations of metallic Ru. The lattice parameters of the well-crystallized samples were $a = 5.55$ Å and $c = 7.12$ Å. Compared to $LaRu_3Si_2$,[12] the Ce-based compound has the same c parameter, but a slightly (2%) smaller a parameter. Since both x-ray diffraction and resistivity measurements show that annealing at 1000 °C leads to a segregation of the samples into the tetragonal system $CeRu_2Si_2$ (Ref. 13) and elemental Ru, the samples for the present study were kept unannealed.

Figure 1 shows that the resistivity of $CeRu_3Si_2$ increases monotonically from the residual resistivity $\rho_0 = 13$ $\mu\Omega$ cm at 4.2 K to $\rho \simeq 67$ $\mu\Omega$ cm at 300 K. An inflection point exists in $\rho(T)$ near $T = 20$ K. The susceptibility of $CeRu_3Si_2$ is weakly paramagnetic above 100 K and shows an upturn at lower temperatures (Fig. 2). The same data, replotted as χT vs T, follow a straight line $\chi T = \chi_0 T + C_i$ above 100 K (inset). This can be understood if one assumes that (1) the (intrinsic) susceptibility of $CeRu_3Si_2$ is temperature independent, $\chi_0 = (9.4 \pm 0.7)\times10^{-4}$ emu/mole Ce, and (2) paramagnetic impurities contribute to a term $\chi_i = C_i/T$. The value $C_i = (1.8 \pm 1.0)\times10^{-2}$ K emu/mole Ce implies that the concentration of the most probable species of magnetic "impurities," i.e., free Ce^{3+} ions carrying full moments, is 2 ± 1 at.%. The nonlinear behavior found below 100-K points to magnetic interactions between these "impurities."

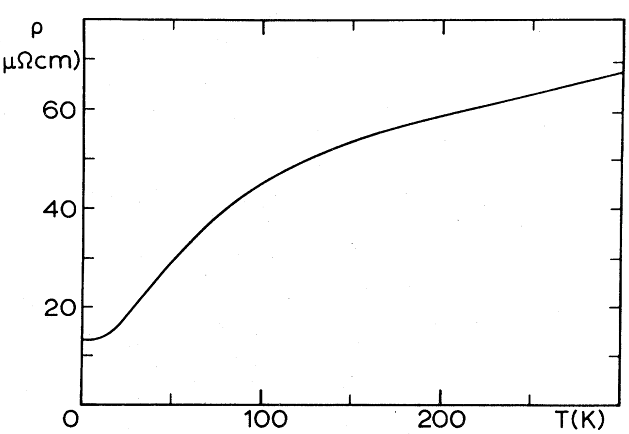

FIG. 1. Resistivity of $CeRu_3Si_2$ (sample no. 1) as a function of temperature.

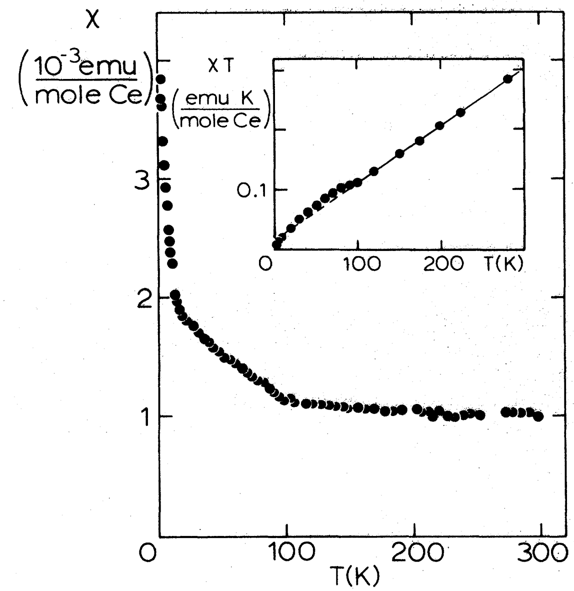

FIG. 2. Temperature dependence of the susceptibility of $CeRu_3Si_2$ (sample no. 1). Inset shows for a few of these data points χT vs T.

The enhanced Pauli-type susceptibility χ_0 of $CeRu_3Si_2$ is considerably lower than that of the weakly MV systems $CeSn_3$ and $CePd_3$ [$\chi_0 = (14.6\text{–}14.7)\times 10^{-4}$ emu/mole Ce],[14] but considerably higher than that of strongly MV $CeRu_2$($\chi_0 \simeq 6.2\times 10^{-4}$ emu/mole Ce).[2]

Following Ref. 15, we can define a "spin-fluctuation temperature" T_{sf}, by plotting $\tilde{\mu}(T) = \chi_0 T/C$, with $C = 0.807$ K emu/mole Ce, as a function of temperature on a logarithmic scale, and taking T_{sf} from $\tilde{\mu}(T_{sf}) = 0.5$. For $CeSn_3$ one finds $T_{sf} \simeq 270$ K, while $T_{sf} \simeq 440$ K and $\simeq 700$ K are extrapolated for $CeRu_3Si_2$ and $CeRu_2$, respectively.

The specific heat of $CeRu_3Si_2$ for $0.5\text{ K} < T < 5\text{ K}$ is shown in Fig. 3 in a plot C/T vs T^2. For $T > 2$ K we find $C = \gamma T + \beta T^3$ with $\gamma = 39 \pm 1$ mJ/mole K^2 and $\beta = 0.8 \pm 0.1$ mJ/mole K^4. While the latter coefficient yields a low-temperature value for the Debye temperature of $\theta_D = 245 \pm 10$ K, the coefficient γ is close to that found for $CePd_3$ (37 mJ/mole K^2) and intermediate between $\gamma = 53$ mJ/mole K^2 of $CeSn_3$ (Ref. 14) and $\gamma = 23$ mJ/mole K^2 of $CeRu_2$ (Ref. 6). This indicates a density of states at the

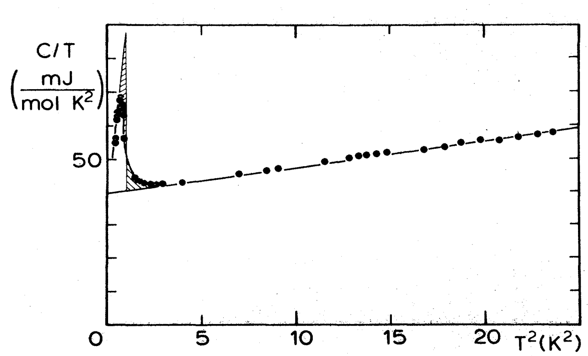

FIG. 3. Temperature dependence of the specific heat of $CeRu_3Si_2$ (sample no. 2) in a plot C/T vs T.

Fermi level, $N(E_F)$, dressed by the electron-phonon coupling, which amounts to $N(E_F) \simeq 1.4$ states/eV at spin for $CeRu_3Si_2$.

The low-temperature properties discussed above characterize $CeRu_3Si_2$ as a MV system intermediate between the prototypical MV systems $CeSn_3$ and $CePd_3$ on the one hand and strongly MV $CeRu_2$ on the other. The dimensionless ratio of the measured values of χ_0 and γ is

$$R = (\mu_0^{-1}\chi_0/\gamma)[\pi^2 k_B^2/g_J^2 J(J+1)] = 0.8 \pm 0.1 ,$$

where μ_0 is the induction constant, k_B Boltzmann's constant, $g_J = \frac{6}{7}$ the Landé g factor, and $J = \frac{5}{2}$ the quantum number of the total angular momentum for Ce^{3+}. As for many other MV compounds we find R for $CeRu_3Si_2$ to be of order unity, which proves the low-temperature phase of such a system to behave as a noninteracting Fermi gas.[14]

$CeRu_3Si_2$ becomes superconducting below $T_c \simeq 1$ K. This is demonstrated by a discontinuity in the specific heat (Fig. 3), a large diamagnetic signal in the low-frequency (119 Hz) ac susceptibility [Fig. 4(a)], and the expulsion of magnetic flux (dc Meissner effect) from a large fraction (65%) of the sample volume. The Meissner experiment was done by measuring the dc magnetization of a powdered piece of the sample, while cooling it in a small magnetic field to well below T_c.

From the different transition temperatures T_c (as $B \rightarrow 0$) that are obtained by ac susceptibility as well as the volume techniques dc magnetization (1.25 and 0.97 K, respectively, for sample no. 1) and specific heat ($T_c \approx 0.98$ K, sample no. 2) we infer that $CeRu_3Si_2$ is an inhomogeneous type-II superconductor. If such a material becomes cooled to below T_c, paramagnetic flux remains partly frozen in (at pinning centers or other trapping regions) and, thus, the diamagnetic magnetization is reduced. The "Meissner volume" provides, then, only a lower bound of the superconducting part of the volume. From the observed large Meissner volume we can, therefore, conclude a large fraction ($\geqslant 65\%$) of the sample volume to be superconducting. Bulk superconductivity of $CeRu_3Si_2$ is supported by the large specific-heat jump $\Delta C \simeq 1.1\gamma T_c$,[16] which is of the same order as that predicted by the BCS theory ($1.43\gamma T_c$). Both the small ratio $T_c/\theta_D \simeq 2.5\times 10^{-2}$ and the magnitude of the reduced

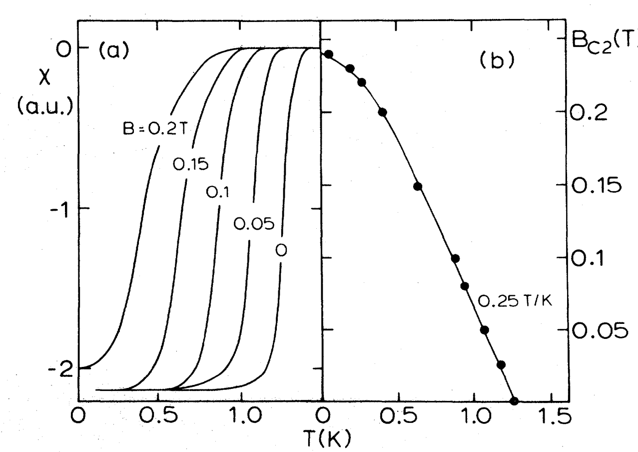

FIG. 4. (a) Inductive transitions as a function of external magnetic field for $CeRu_3Si_2$ (sample no. 1). (b) Upper critical field as determined from (a) as a function of temperature.

specific-heat jump $\Delta C/\gamma T_c$ suggest $CeRu_3Si_2$ to be a conventional weak-coupling (BCS) superconductor.

As is seen in Fig. 4(a), the application of a magnetic field shifts the normal-to-superconducting transition towards lower temperatures. By plotting the applied field versus the midpoint of the corresponding transition curve, one gets the temperature dependence of the critical field. The size of this critical field ($B_{C2} \lesssim 0.24T$) proves the type-II behavior inferred above. The absolute value of the slope of the upper critical field versus temperature dependence at T_c, $B'_{C2} = -(dB_{C2}/dT)_{T_c}$, is about 0.25 T/K for $CeRu_3Si_2$. This is comparable to B'_{C2} of many type-II superconductors with similar T_c, but smaller by one to two orders of magnitude than the critical field slope as observed[17] for the heavy-fermion system $CeCu_2Si_2$ (with lower T_c). By comparing the specific-heat jump height ΔC with B'_{C2}, we can estimate the Ginzburg-Landau parameter $\kappa \simeq 6$ (cf. Ref. 17). With this κ and the orbital critical field at $T=0$, $B^*_{C2}(0) \simeq 0.69 B'_{C2} T_c \simeq 0.17$ T, both the thermodynamic and lower critical fields can be estimated (as $T \rightarrow 0$), yielding $B_{C\mathrm{th}}(0) \simeq 17$ mT and $B_{C1}(0) \simeq 3.4$ mT.

In summary, $CeRu_3Si_2$ appears to be a MV system with low-temperature properties intermediate between those of weakly MV systems like $CeSn_3$ and $CePd_3$ and strongly MV systems like $CeRu_2$. For $CeRu_3Si_2$ (with $T_{sf} \simeq 440$ K) we found superconductivity below $T_c \simeq 1$ K, which is much smaller than $T_c \simeq 7$ K of the La homolog. For comparison, in the case of $CeRu_2$ (with $T_{sf} \simeq 700$ K) T_c is about twice as large as T_c of $LaRu_2$, whereas $CeSn_3$ ($T_{sf} \simeq 270$ K) is not superconducting despite $T_c \simeq 6$ K of $LaSn_3$. This seems to demonstrate that upon decreasing the strength of the hybridization the magnetic character and, hence, the pair-breaking capability of the Ce ions steadily increases.[18] More superconducting MV systems should be searched for to verify this interesting correlation which would, of course, imply superconductivity to become extremely unlikely in the case of a nearly trivalent Kondo-lattice system (with $T_{sf} \simeq 10$ K). Thus, the observed superconductivity in $CeCu_2Si_2$ requires a new pairing mechanism, that is (1) probably originating[19] in the narrow Kondo (many-body) resonance at E_F and (2) strong enough to overcompensate all kinds of pair-breaking processes. Only such a new pairing mechanism can explain that $CeCu_2Si_2$ is a superconductor, while $LaCu_2Si_2$ is not.

The work at Darmstadt was supported by the Sonderforschungsbereich 65 Frankfurt–Darmstadt and that at Polytechnic in part by the National Science Foundation under Grant No. DMR-8202726.

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*Present address: E. R. 209-CNRS, 1 Place A. Briand, F-92190 Meudon, France.

†Present address: Tata Institute of Fundamental Research, Bombay 400 005, India.

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