Superconductivity in $CeCu_2Si_2$ Single Crystals

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$CeCu_2Si_2$ single crystals prepared with an excess of Cu exhibit low residual resistivity ρ_0, low susceptibility χ, small unit-cell volume V, and bulk "heavy-fermion" superconductivity below 0.65 K, while crystals grown from stoichiometric melt show higher ρ_0 and χ, larger V, but no superconductivity. $CeCu_2Si_2$ behaves as an s-state superconductor with strongly temperature-dependent pair breaking and almost isotropic Fermi surface.

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The Kondo-lattice system $CeCu_2Si_2$ has been considered the first metallic analog to liquid ^{3}He, because it shows a phase transition at $T_c \gtrsim 0.5$ K from a "Fermi-liquid" state into a superconducting (sc) state, which is carried by pairs of "heavy fermions" presumably generated by interactions between the localized $4f$ electrons and the conduction electrons.[1] Challenging problems are posed by this system to both theorists and experimentalists: (1) A microscopic understanding of the exotic low-temperature properties of $CeCu_2Si_2$ is still lacking. (2) It is not clear if the Cooper pairs in $CeCu_2Si_2$ are in a singlet state like in all other superconductors known or in a triplet state like in ^{3}He. (3) The phase diagram of $CeCu_2Si_2$ has not yet been determined, so that one does not understand why its transition temperature depends so sensitively on preparation[2] and stoichiometry.[3,4] In particular, $CeCu_2Si_2$ single crystals prepared from stoichiometric melts do not superconduct at ambient pressure,[5-8] but surprisingly do so under an external pressure $p \geq 1$ kbar.[5] Moreover, for polycrystalline $CeCu_2Si_2$ a wide scatter of T_c's has been observed.[6] This has been attributed to the action of a strong, as yet unknown, pair-breaking mechanism which is accompanied, for $T_c < 0.5$ K, by both a moderate reduction of the Kondo temperature and disappearance of the sc gap.[6]

Because of the aforementioned metallurgical difficulties, however, results on $CeCu_2Si_2$ are often considered with severe skepticism. Therefore, it was an urgent task to study the properties of sc $CeCu_2Si_2$ single crystals, which could recently be grown by use of an excess of Cu,[4] and compare them with those of non-sc single crystals and previous results[6] on polycrystalline samples. The latter were found[9] to exhibit extremely large slopes $B_{c2}' = -|dB_{c2}/dT|_{T_c}$ of the upper critical field curves at T_c and it was concluded that such a large B_{c2}' value is a typical signature of a "heavy-fermion" superconductor and is not caused by anisotropy effects due to the quasi two-dimensional structure of $CeCu_2Si_2$. Obviously, this essential conclusion had to be verified by measuring the orientation dependence of B_{c2}' of single crystals.

For the present study, several $CeCu_2Si_2$ single crystals with typical dimensions $1\times 1\times 0.1$ mm^3 were grown by the Bridgman technique, using Al_2O_3 crucibles, from melts with varying composition, i.e., Ce:Cu:Si = $1:2(1+x):2$. The starting materials were prereacted in an argon-arc furnace and homogenized in a cold crucible before growth. $CeCu_2Si_2$ melts incongruently at $T_m = 1545\,°$C as determined by differential thermal analysis.[3,10] No phase transition was detected between T_m and 300 K.[10] We will discuss below the properties of single crystals grown from melts with $x = 0$ (No. 1), $x = 26.6\%$ (No. 2), and $x = 30\%$ (No. 3), respectively. Crystal No. 3 was investigated "as grown" and Nos. 1 and 2 after annealing for four days at 1000 °C.

The crystals have been characterized by electron-probe microanalysis and x-ray fluorescence. Within the resolution of these techniques (± 5% per element) no significant deviations from the 1:2:2 composition could be resolved. Structure refinement using a four-circle x-ray diffractometer was done on cube-shaped single crystals, which were cut from the same charges as crystals No. 1 and No. 2. For both crystals the electron density at the Cu sites was found to correspond to only (90± 5)% of complete Cu occupation and, thus, to be independent of the composition of the melts too. While the two crystals have the same lattice parameter a [$(4.10\pm 0.01)\times 10^{-10}$ m], their c parameters are slightly different [$(9.96\pm 0.01)\times 10^{-10}$ m for No. 1 and $(9.93\pm 0.01)\times 10^{-10}$ m for No. 2].

The specific heat $C(T)$, upper critical field, and resistivity $\rho(T)$ for these $CeCu_2Si_2$ single crystals are presented in Figs. 1, 2, and 3, respectively. Crystals grown from stoichiometric melt (No. 1) do not superconduct above $T=0.02$ K. However, the bulk of those crystals grown with Cu excess (No. 2 and No. 3) becomes sc below $T_c=0.65-0.69$ K as clearly demonstrated by a substantial dc Meissner effect,[4] and a large specific-heat jump, $\Delta C=1.27\gamma(T_c)T_c$. The values of both $\gamma(T_c)=C_n(T_c)/T_c=0.73$ J/mol$\cdot$K^2 and of the coefficient $A\simeq 10^{-7}$ Ω mK^{-2} of the quadratic term in the low-T resistivity (inset of Fig. 3) are comparable to the giant numbers previously obtained with polycrystalline samples.[1,2] These observations indicate the existence of heavy fermions which are responsible for the superconductivity (sc) in $CeCu_2Si_2$, independent of the crystallinity of the samples.

Besides the large ΔC value, we also find very large critical-field slopes. This is shown in Fig. 2 for crystal No. 3, exhibiting $B_{c2}'\simeq 23$ T K^{-1}, a value that is even larger than those reported for polycrystals.[9] In contrast to findings on layered superconductors like $NbSe_2$, which exhibit much higher B_{c2}' when the field is applied parallel ($B_{c2\parallel}'$) rather than perpendicular ($B_{c2\perp}'$) to the layers,[13] for $CeCu_2Si_2$ this slope is almost independent of the orientation of the external field relative to the Ce planes. Since $B_{c2}'(T\to T_c)$ is determined by the "orbital pair-breaking effect" of the external field,[14] namely through the fermions' velocity and transport scattering length only,[9] our observation implies an almost isotropic Fermi surface in the renormalized (Fermi-liquid) state of $CeCu_2Si_2$. This is supported by the observed isotropy in the residual resistivities. Interestingly enough, recent band-structure calculations[15] reveal that also the nonrenormalized Fermi surface of $CeCu_2Si_2$ is rather isotropic, in accordance with our observation that $\rho(T)$ is almost orientation independent as $T\to 300$ K (cf. Fig. 3).

If we now consider the range $T<0.6$ K, where $B_{c2}(T)$ begins to deviate from linear behavior, we find $B_{c2\parallel}$ to be lower than $B_{c2\perp}$. This could reflect anisotropy either in the electron-phonon coupling,[16] or alternatively in the "paramagnetic pair-breaking effect" due to the external field. In the latter case an anisotropic spin-orbit scattering rate would have to be invoked.[14] Note that also the low-temperature peak in $\rho(T)$ at $T_\rho=5-20$ K, originating in the maximum (incoherent) conduction-electron scattering from the crystal-field (CF) ground states of Ce^{3+},[11] shows considerable anisotropy (Fig. 3). We wish to stress, however, that none of the aforementioned anisotropies contradicts our conclusion of an almost isotropic Fermi surface.

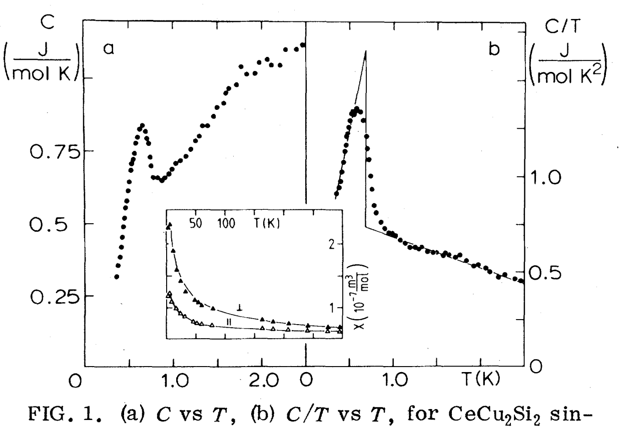

FIG. 1. (a) C vs T, (b) C/T vs T, for $CeCu_2Si_2$ single crystal No. 2, as well as $\chi_\parallel$ vs T, $\chi_\perp$ vs T (inset) for crystal No. 1, after a 17-day annealing. $\chi_\parallel$, $\chi_\perp$ were corrected for the demagnetizing factors, $N_\parallel=0.68$, $N_\perp=0.15$. Solid lines in the inset represent $\chi=\tilde{\chi}/(1+\lambda\tilde{\chi})$; $\tilde{\chi}_\parallel(T)$, $\tilde{\chi}_\perp(T)$ were calculated from the crystal-field scheme (Ref. 11); $\lambda_\parallel(T)$, $\lambda_\perp(T)$ as in Ref. 12.

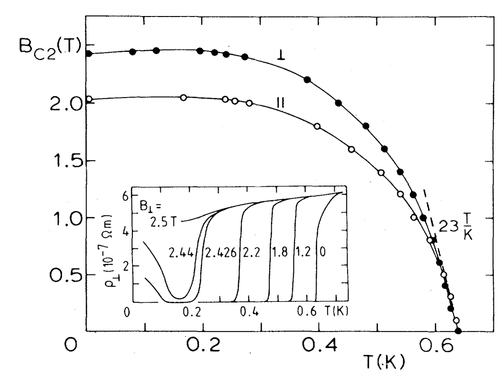

FIG. 2. B_{c2} vs T, as obtained from the midpoints of ρ vs T curves taken at different external fields for $CeCu_2Si_2$ single crystal No. 3. Field B and current are aligned to each other, either parallel ($B_{c2\parallel}$, $\rho_\parallel$) to or perpendicular ($B_{c2\perp}$, $\rho_\perp$) to Ce planes. Inset shows $\rho_\perp$ vs T at differing fields for this crystal.

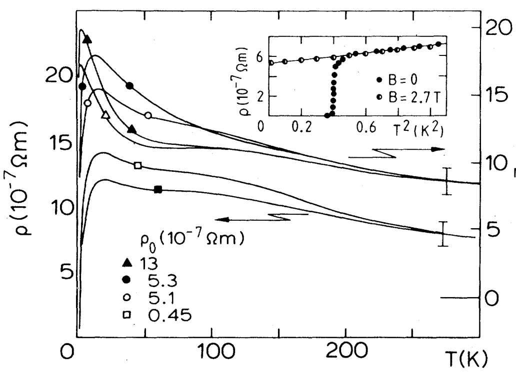

FIG. 3. ρ vs T for two annealed $CeCu_2Si_2$ single crystals, No. 1 (triangles) and No. 2 (squares), and one unannealed crystal, No. 3 (circles). $\rho_\perp$: closed, $\rho_\parallel$: open symbols. Inset shows low-temperature data for crystal No. 3 in a plot of $\rho_\perp$ vs T^2.

The data of Fig. 2 display a flat maximum near $T = 0.2$ K in both $B_{c2\parallel}(T)$ and $B_{c2\perp}(T)$. Thus, when cooled in a field B slightly below the peak value, $CeCu_2Si_2$ shows "reentrant" behavior, that is sc occurs only in an intermediate temperature range (see inset). Corresponding minima are visible in the temperature dependence of the ac susceptibility for single crystals and, though less pronounced, in that of the resistivity of polycrystalline samples. Such a $B_{c2}(T)$ maximum cannot be explained by pair breaking due to the external field. Rather, it points to an additional, *temperature-dependent* pair-breaking mechanism, presumably the same mechanism that causes "gapless sc" in polycrystals with $T_c < 0.5$ K, as concluded from specific-heat results.[6] Among other possible explanations for this effect we mention (1) exchange-enhanced "polarization fields" between (residual) Ce moments,[17] (2) "Kondo-type" pair breaking from these residual moments,[18] and (3) competition of the (phonon-mediated) attraction and the Coulomb repulsion between those slowly moving heavy fermions whose velocity is already comparable to the velocity of sound.[6]

In the remainder of this paper we compare properties of sc and non-sc single crystals. Figure 3 confirms literature results[5,8] on *non-sc*-crystals, i.e., a low value of T_ρ ($\simeq 5$ K) and an enormously high residual resistivity ρ_0 ($\simeq 1.3 \times 10^{-6}$ Ω m). Since T_ρ is considered a measure of the Kondo temperature T_K,[19] the low T_K value might be relevant for the suppression of sc in crystal No. 1.[4] In fact, the sc single crystals show $T_\rho \simeq 20$ K which is comparable to T_ρ of sc polycrystals.[4] Moreover, after a four-day annealing, ρ_0 of the sc crystal No. 2 is about 30 times smaller than ρ_0 of the non-sc one. It suggests that the sc single crystals, though prepared with a Cu excess, have a more nearly perfect lattice. These conclusions illustrated here on three samples are supported by observations on several other crystals.

We would like to note, however, that there is no obvious correlation between T_c and ρ_0: For crystal No. 1 a 17-day annealing, although reducing ρ_0 to 4.4×10^{-7} Ω m, failed to induce sc, whereas the unannealed crystal No. 3 with $\rho_0 \simeq 5 \times 10^{-7}$ Ω m did superconduct. Therefore, it appears unlikely to us that $CeCu_2Si_2$ is a p-wave superconductor, for which a strong inverse correlation should exist between T_c and ρ_0.[20] To support this conclusion we have measured for crystals No. 1 and No. 2 the susceptibilities parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the Ce planes (inset of Fig. 1). For both crystals, $\chi(T)$ is dominated by the *single ion* anisotropy of the $4f$ wave function and shows rather flat peaks near 3.5 K, with $\chi_\perp/\chi_\parallel \sim 2$. The average peak susceptibility $\bar{\chi}_0 = (2\chi_{0\parallel} + \chi_{0\perp})/3$ is $(7 \pm 3) \times 10^{-8}$ m^3/mol for the sc crystal (No. 2), in good agreement with previous results on sc polycrystals.[2] On the other hand, for the non-sc crystal (No. 1) $\bar{\chi}_0$ is more than twice as large, i.e. $(17.0 \pm 0.3) \times 10^{-8}$ m^3/mol.[21] Comparison of the former value with the measured specific-heat coefficient for crystal No. 2, $\gamma \simeq \gamma(T_c) = 0.73$ J/mol$\cdot$K^2, yields the same ratio[22] $R = (\bar{\chi}_0/\chi_{\rm Pauli})/(m^*/m_0) = (1 + B_0)^{-1} = (\bar{\chi}_0/\gamma)/(3\,\mu_0\mu_B^2/\pi^2 k_B^2) \sim 0.5$ as for sc polycrystals.[2] Thus, the heavy-fermion superconductor $CeCu_2Si_2$ shows a Landau parameter $B_0 \simeq +1$, whereas this should be close to -1 for a p-wave superconductor with $T_c \sim 0.5$ K (Ref. 23).

Further comparison between sc and non-sc crystals reveals differences not only in $\bar{\chi}_0$, but also in the unit-cell volume $V = a^2c$. For polycrystals with varying stoichiometry it was found[3,4] that T_c increases steadily as $V = a^2c$ increases from $\simeq 1.66 \times 10^{-28}$ m^3 until, at $V_{cr} \simeq 1.67 \times 10^{-28}$ m^3, there is a precipitous drop of T_c, and no sc is found for $V > V_{cr}$. All available results on single crystals fit into this scheme: Non-sc crystals from the literature[7,8] and crystal No. 1 show $V > V_{cr}$, while crystal No. 2 shows $V < V_{cr}$. Employing the large bulk modulus of this material ($\simeq 10^3$ kbar, Ref. 24), we estimate that the 0.3% decrease in volume on going from crystal No. 1 to No. 2 corresponds to an increase in "internal pressure" of a few kilobars. Pressures of this order, however, were found to induce sc in otherwise non-sc single crystals.[5]

In summary, the results of this work suggest that (1) the Fermi surface of $CeCu_2Si_2$ is rather isotropic, particularly in its Fermi-liquid ($T < T_K$) phase, and (2) the observed change from superconducting to nonsuperconducting is driven by a strongly temperature-dependent pair-breaking mechanism, which is accompanied by a considerable increase of the susceptibility and small volume changes near a critical value V_{cr}. We have demonstrated that the bulk of high-quality $CeCu_2Si_2$ single crystals shows the same unusual low-temperature, notably superconducting, properties as earlier discovered for polycrystalline material and, in addition, that $CeCu_2Si_2$ very likely is not a triplet superconductor. Because of the recent discovery[25] of "heavy-fermion" superconductivity in UBe_{13}, this phenomenon should be considered a more general one.

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[12]The quantities

$$\lambda_{\parallel}(T) \simeq Z^{-1}\{(1.15 + 3.41) \times \exp[(-66\text{ K})/T]\} \times 10^7$$

and

$$\lambda_{\perp}(T) \simeq Z^{-1}\{(3.8 + 1.6) \times \exp[(-66\text{ K})/T]\} \times 10^6$$

(in mol/m^3), with Z being the partition function, comprise Kondo correlations (Ref. 15) and anisotropic exchange interactions; see also J. Aarts, F. R. de Boer, and D. E. MacLaughlin, to be published.

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