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# Critical Fields of the "Heavy-Fermion" Superconductor $CeCu_2Si_2$

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Measurements are reported of the lower and upper critical fields, $B_{c1}(T)$ and $B_{c2}(T)$, of $CeCu_2Si_2$. The observed, extremely high values of the slope $(-dB_{c2}/dT)_{T_{c0}}$ lend strong support to the formation of Cooper pairs by the heavy fermions which exist in the normal state of $CeCu_2Si_2$. Characteristic parameters of the system of heavy fermions are derived.

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Unusual superconducting materials, e.g., Chevrel phases,[1] oxides,[2] or organic conductors,[3] have recently become of great interest in view of potential technical applications and the possibility of nonconventional mechanisms in superconductivity.

The (nearly) trivalent ternary compound $CeCu_2Si_2$ shows well-defined, localized magnetic moments above $T \cong 10$ K (Ref. 4), but approaches a nonmagnetic state below $T \cong 10$ K displaying the properties of a heavy Fermi liquid[5]; e.g., the specific heat was found to be $C \cong \gamma T$, where $\gamma \cong 1$ J mole$^{-1}$ K$^{-2}$ is about a thousand times larger than for simple metals. $CeCu_2Si_2$ becomes superconducting below $T_c \cong 0.6$ K (Ref. 5). The height of the specific-heat jump at $T_c$, comparable to the giant normal-state specific heat, $\gamma T_c$, has led to the conclusion[5] that the superconducting state of $CeCu_2Si_2$ must be of a hitherto unknown kind, in that its Cooper pairs are formed by quasiparticles of very large effective mass (heavy fermions). In fact, the reference system $LaCu_2Si_2$, showing usual metallic behavior, does not become superconducting.[5]

To further support $CeCu_2Si_2$ being the first heavy-fermion superconductor, we present in this Letter results of the lower and upper critical fields, $B_{c1}(T)$ and $B_{c2}(T)$. Special emphasis has been put on the slope of $B_{c2}(T)$ at $T_c$, which should reflect[1] the high $\gamma$ coefficient. Analysis of these data will be used to estimate the key parameters of the normal Fermi-liquid state.

A wide scatter of $T_c$'s has been reported for polycrystalline samples of $CeCu_2Si_2$, ranging from $<0.06$ K (Ref. 6) to 0.65 K (Ref. 7). As was recently shown,[8] however, $T_c \cong 0.55 \pm 0.15$ K can always be achieved by powdering and subsequent proper heat treatment. On the other hand, no superconductivity has so far been observed for $CeCu_2Si_2$ single crystals.[8,9] This might be due to a considerable ($\cong 20\%$) deficiency in Cu occupation, as established for one of those single crystals.[8] For the present investigations, two polycrystalline bulk samples were used. One of them (No. 7) was annealed at 1100 °C and found to be very clean,[7] while the other one (No. 4), annealed at only 900 °C, was less clean.[10]

Figure 1 shows the field dependence at constant temperatures of the magnetization $M$ for sample No. 7, which exhibits a static Meissner effect corresponding to 60% of the volume, when measured in powder form.[7] $M$ was measured by using a superconducting flux transformer between the sample and a flux-gate magnetometer (Hewlett-Packard Model 428B). In the inset, the initial slopes of these $M(B)$ curves are plotted as a function of temperature. The magnetization curves show broad maxima, probably caused by a broad distribution of demagnetizing fields within the polycrystalline sample. In such a situation, a lower

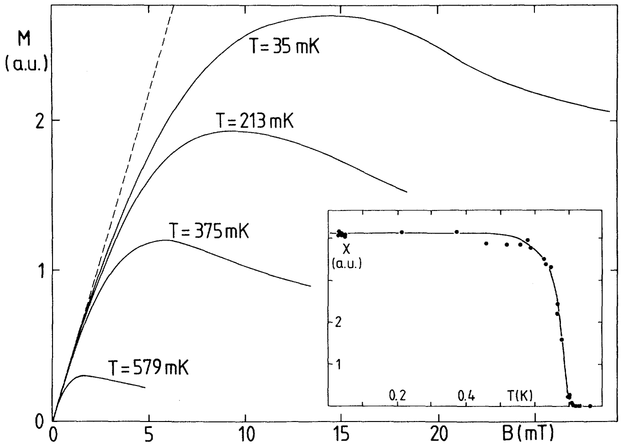

FIG. 1. dc magnetization, $M$, of $CeCu_2Si_2$ (No. 7) as a function of the external magnetic field, $B$, at different temperatures. Inset shows low-field slopes of $M(B)$ curves vs temperature.

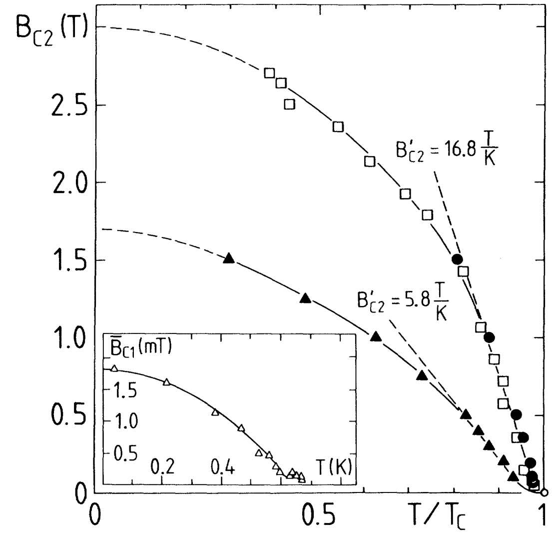

FIG. 2. Upper critical field, $B_{c2}$, of $CeCu_2Si_2$ as a function of the reduced temperature, $T/T_c$. While $T_c$ is the transition temperature at $B_c = 0$ as *measured*, $T_{c0}$ is defined by *extrapolation* of linear $B_{c2}(T)$ dependence to $B = 0$. Data were obtained from ac susceptibility (triangles: No. 7, $T_{c0} = 0.64$ K; squares: No. 4, $T_{c0} = 0.66$ K) or specific heat (circles: No. 4, $T_{c0} = 0.56$ K). Inset shows $\overline{B}_{c1}$ vs $T$ (No. 7) as explained in the text.

bound of the lower critical field is provided by $B_{c1} \cong \overline{B}_{c1}/(1-D)$ where $\overline{B}_{c1}$, plotted in the inset of Fig. 2, is the field at which the first deviation from the low-field linear $M(B)$ dependence occurs. The demagnetization factor, $D \cong 0.20$, of sample No. 7 was experimentally determined with a Cd sample of the same geometry ($4.1 \times 2.1 \times 2.0$ $mm^3$). Figure 2 shows the temperature dependence of $B_{c2}$ as determined from the midpoints of either inductive or calorimetric transitions for both samples.

We shall discuss the results on the clean $CeCu_2Si_2$ sample No. 7 first. When the data in Fig. 2 are extrapolated to $T=0$, we find $\overline{B}_{c1}(0) \simeq 1.8$ mT, resulting in $B_{c1}(0) \simeq 2.3$ mT and $B_{c2}(0) \simeq 1.7$ T. This clearly indicates type-II behavior with a large Ginzburg-Landau (GL) parameter $\kappa$. For example, in proportion to the relatively low $T_c$, $B_{c2}(0)$ is comparable to that of Chevrel-phase superconductors.[1] An upward curvature is observed at low fields for both $B_{c2}(T)$ and $B_{c1}(T)$, presumably caused by inhomogeneities in the samples. For $B_{c2}(T)$, we obtain from the linear region $(-dB_{c2}/dT)_{T_{c0}} \equiv B_{c2}' = 5.8$ T/K, which is comparable to the highest values found for Chevrel-phase superconductors.[1]

In the following, we shall attempt to analyze this initial slope by using an expression which has been successfully applied to $A15$ superconductors.[11] Ignoring possible anisotropy effects in the polycrystalline $CeCu_2Si_2$ samples, we shall *assume* a spherical Fermi surface determined by a mean Fermi wave number $k_F$, yielding[11]

$$B_{c2}' \simeq \left(7.95\times10^{32}\,\frac{\mathrm{T\,m^2K^2}}{\mathrm{J^2}}\right)\frac{\gamma T_c}{k_F{}^4} + \left(4780\,\frac{\mathrm{T\,K\,m^2}}{\Omega\mathrm{J}}\right)\gamma\rho_0. \qquad (1)$$

Inserting into Eq. (1) *measured*[7] data for $T_c$ ($=0.64$ K), the residual resistivity $\rho_0$ ($=3.5\times10^{-8}$ $\Omega$ m), and the giant (heavy-fermion derived) coefficient $\gamma$ ($\simeq 2.0\times10^4$ J $K^{-2}$ $m^{-3}$, with $V_{\text{mole}} \simeq 5.03 \times 10^{-5}$ $m^3$), we obtain $k_F \simeq 1.7\times10^{10}$ $m^{-1}$. Probably because of anisotropy effects, this is slightly larger than $k_F \simeq 1.6\times10^{10}$ $m^{-1}$ of the ordinary conduction-electron gas as previously estimated from the maximum high-temperature resistivity.[12] The latter $k_F$ value corresponds to a reasonable valence-electron concentration of about 2/atom. We conclude that both the ordinary conduction-electron gas at high temperature and the low-temperature Fermi-liquid phase can be described by similar mean values of the Fermi wave number. This strongly suggests a description of the Fermi-liquid phase in $CeCu_2Si_2$ in the spirit of Landau's phenomenological theory,[13] i.e., by assuming some strong interaction between conduction electrons which leaves the Fermi wave number unchanged but *dramatically renormalizes the properties of the conduction-electron states near* $k_F$. For example, the Fermi velocity of the quasiparticles, $\bar{v}_F \simeq (6.02\times10^{-13}\ \mathrm{J\,K^{-2}\,s^{-1}})\bar{k}_F{}^2\gamma^{-1} \simeq 8.7\times10^3\ \mathrm{m\,s^{-1}}$, and their effective mass, $m^* = \hbar\bar{k}_F\bar{v}_F{}^{-1} \simeq 220m_0$, differ by two orders of magnitude from the corresponding free-electron values. We wish to stress that, because of the measured $B_{c2}'$ value, this Fermi-liquid phase *cannot* be attributed to a narrow $4f$ band originating from one tightly bound electron per Ce ion,[14] since this would imply a much too small $\bar{k}_F$, i.e., $\simeq 0.7\times10^{10}\ \mathrm{m^{-1}}$ (associated with $\bar{v}_F \simeq 1.5\times10^3\ \mathrm{m\,s^{-1}}$ and $m^* \simeq 530m_0$).

The estimation of some important parameters, which characterize the novel superconducting state of $CeCu_2Si_2$, is also straightforward. Using relations given in Ref. 11 and the above values for $T_c$, $\rho_0$ and $\gamma$, we find the BCS coherence length $\xi_0 \simeq 1.9\times10^{-8}$ m. This is comparable to the mean free path of the quasiparticles, $l \simeq 1.2\times10^{-8}$ m. The London penetration depth (as $T\to0$) assumes an unusually high value, i.e., $\lambda \simeq 2\times10^{-7}$ m. The GL parameter is estimated to be $\kappa \simeq 22$ for sample No. 7 and $\simeq 10$ in the "pure limit" ($l \gg \xi_0$).

With use of this $\kappa$ value, the above analysis of the initial slope of $B_{c2}(T)$ can now be supported by the calculation of certain quantities for sample No. 7 and comparing them with the corresponding quantities as either directly measured or calculated from the results of other experiments. For this purpose, we first estimate[1] the "orbital critical field" (as $T\to0$), i.e., $B_{c2}{}^*(0) \simeq 0.69B_{c2}'\times T_c \simeq 2.6$ T. This is about 50% higher than $B_{c2}(0)$ as measured, pointing to the presence of other pair-breaking mechanisms like Pauli paramagnetic limiting or exchange scattering from paramagnetic impurities. Now we can estimate the thermodynamic critical field (as $T\to0$) from (i) $B_{c2}{}^*(0)$ and (ii) the specific-heat coefficient $\gamma$ [assuming a parabolic $B_{cth}(T)$ dependence]. We find almost the same values, namely (i) $B_{cth}(0) = B_{c2}{}^*(0)/\sqrt{2}\,\kappa_1(0) \simeq 66$ mT [with $\kappa_1(0) \simeq 1.26\kappa$ (Ref. 15)] and (ii) $B_{cth}(0) = [7.65\times10^{-4}(\mathrm{m^3/J})^{1/2}]\gamma^{1/2}T_c \simeq 69$ mT (Ref. 16). This is much higher than $B_{cth}(0) \simeq 3$ mT of the conventional superconductor Cd with comparable $T_c$. Since $B_{cth}(0)$ determines the "condensation energy" of a superconductor, we find the superconducting state of $CeCu_2Si_2$ to be of much higher thermodynamic stability than its conventional counterpart. This is caused by the extremely high density of Cooper-pair states, which tracks the giant $\gamma$ coefficient, in the former material.

With $B_{cth}(0)$ and $\kappa$ we can also estimate the lower critical field through $B_{c1}(0) = B_{cth}(0)\ln\kappa_3(0)/\sqrt{2}\,\kappa_3(0) \simeq 6$ mT, where $\kappa_3(0) = 1.15\kappa$ was used.[15] $B_{c1}(0)$ agrees within an order of magnitude with the measured value ($\simeq 2.3$ mT), which may be considered to be satisfying enough, especially if one keeps in mind the difficulties in measuring $B_{c1}(0)$.

Finally, we are able to estimate the size of the specific-heat jump at $T_c$, namely $\Delta C \simeq (6.86\times10^5\ \mathrm{J\,T^{-2}\,m^{-3}})(2\kappa^2-1)^{-1}T_cB_{c2}'^2 \simeq 1.53\times10^4\ \mathrm{J\,K^{-1}\,m^{-3}}$, which is very close to the experimental value, $\Delta C = 1.59\times10^4\ \mathrm{J\,K^{-1}\,m^{-3}}$ (Ref. 7). These thermodynamic relations give strong evidence that the Fermi-liquid phase of $CeCu_2Si_2$ is formed by renormalized conduction-electron states in the vicinity of $\bar{k}_F = (1.6-1.7)\times10^{10}\ \mathrm{m^{-1}}$, and they disprove, again, the picture of one $4f$-derived heavy fermion per Ce ion[14]; for in this case $\bar{k}_F \simeq 0.7\times10^{10}\ \mathrm{m^{-1}}$ results in $\xi_0 \simeq 3\times10^{-9}$ m, $\lambda \simeq 3\times10^{-7}$ m, and $\kappa \simeq 100$, which is much too large a value.

Having found consistency in the various results for the pure sample No. 7, we now turn to the $B_{c2}$ data of sample No. 4. As is shown in Fig. 2, the initial slope of $B_{c2}(T)$ is 16.8 T/K for this sample, the highest value observed for any superconductor. From the residual resistivity, $\rho_0 \leqslant 4\times10^{-7}\ \Omega$ m (Ref. 17), the mean free path of sample No. 4 is estimated to be much smaller than the coherence length, i.e., sample No. 4 clearly represents the "dirty limit." Using the expression for $B_{c2}'$ in the "dirty limit,"[11] $B_{c2}' = (4.48\times10^3\ \mathrm{T\,K\,m^2\,J^{-1}\,\Omega^{-1}})\gamma\rho_0$, with $\gamma = 1.4\times10^4\ \mathrm{J\,K^{-2}\,m^{-3}}$ (Ref. 10), we estimate $B_{c2}' \leqslant 25$ T/K. Again, there is satisfactory agreement with the experimental result.[18]

To conclude, we have found that (i) the purer $CeCu_2Si_2$ sample shows an initial slope of the upper critical field $B_{c2}(T)$ of the same size ($\simeq 6$ T/K) as $B_{c2}'$ of the best high-field superconductors (with much higher transition temperatures) known so far; this is caused by the very small Fermi velocity of the heavy fermions forming the Cooper pairs in $CeCu_2Si_2$ [in the "pure limit" $B_{c2}' \sim T_c/v_F{}^2$, first term in Eq. (1)]; (ii) a decrease of the quasiparticle mean free path results in a further increase of $B_{c2}'$ to the record value of $\simeq 17$ T/K, which is due to an additional contribution [second term in Eq. (1), $\sim (lv_F)^{-1}$]; (iii) surprisingly enough, possible anisotropy effects,[19] which might originate from the quasi two-dimensional structure of $CeCu_2Si_2$, do not dominate $B_{c2}(T)$ in the *polycrystalline* samples studied, for the reduced specific-heat-jump height is of the order of the BCS value in either case[7,10] and, in addition, the "dirtier," i.e., more isotropic, sample shows the higher $B_{c2}'$ value [providing an *a posteriori* justification of the assumption of a spherical Fermi surface made when using Eq. (1)]; (iv) the low-temperature Fermi-liquid phase of $\mathrm{CeCu_2Si_2}$ is described by a Fermi wave number close to that of the ordinary conduction-electron gas.

The physical origin of both the formation of the extremely heavy fermions and the attractive interaction between the fermions, which constitutes the novel superconducting state of $\mathrm{CeCu_2Si_2}$, remains unknown.

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[18] From $B_{c2}' = 16.8$ T/K we would expect the residual resistivity of the (900 °C) annealed sample No. 4 to be $\rho_0 \simeq 2.7\times10^{-7}$ Ω m, quite a reasonable value.

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