

¹⁰H. Stanley, in *Proceedings of the International Conference on Disordered Systems and Localization*, edited by C. Di Castro (Springer-Verlag, Berlin, 1981), and references therein.

¹¹Y. Gefen, A. Aharony, B. B. Mandelbrot, and S. Kirkpatrick, *Phys. Rev. Lett.* **47**, 1771 (1981).

¹²R. B. Leibovitz, E. I. Alessandrini, and G. Deutscher, *Phys. Rev. B* **25**, 2965 (1982).

Critical Fields of the "Heavy-Fermion" Superconductor CeCu₂Si₂

U. Rauchschwalbe, W. Lieke, C. D. Bredl, and F. Steglich

Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany

and

J. Aarts,^(a) K. M. Martini, and A. C. Mota^(b)

II. Physikalisches Institut, Universität zu Köln, D-5000 Köln 41, West Germany

(Received 12 April 1982)

Measurements are reported of the lower and upper critical fields, $B_{c1}(T)$ and $B_{c2}(T)$, of CeCu₂Si₂. The observed, extremely high values of the slope $(-dB_{c2}/dT)_{T_c}$ lend strong support to the formation of Cooper pairs by the heavy fermions which exist in the normal state of CeCu₂Si₂. Characteristic parameters of the system of heavy fermions are derived.

PACS numbers: 74.60.-w, 72.15.Qm, 74.70.Rv

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 CeCu₂-Si₂ 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 liquid⁵; 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. CeCu₂Si₂ 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, γT_c , has led to the conclusion⁵ that the superconducting state of CeCu₂Si₂ 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 LaCu₂-Si₂, showing usual metallic behavior, does not become superconducting.⁵

To further support CeCu₂Si₂ 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 reflect¹ the high γ 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 CeCu₂Si₂, 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 CeCu₂Si₂ 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

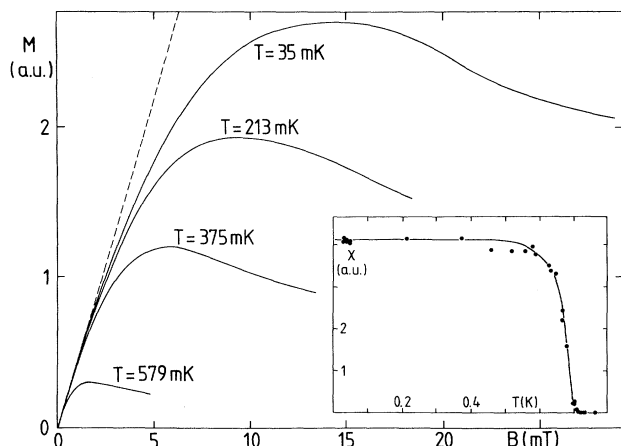


FIG. 1. dc magnetization, M , of CeCu_2Si_2 (No. 7) as a function of the external magnetic field, B , at different temperatures. Inset shows low-field slopes of $M(B)$ curves vs temperature.

bound of the lower critical field is provided by $B_{c1} \cong \bar{B}_{c1}/(1-D)$ where \bar{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 ($4.1 \times 2.1 \times 2.0$ mm³). 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 $\text{CeCu}_2\text{-Si}_2$ sample No. 7 first. When the data in Fig. 2 are extrapolated to $T=0$, we find $\bar{B}_{c1}(0) \cong 1.8$ mT, resulting in $B_{c1}(0) \cong 2.3$ mT and $B_{c2}(0) \cong 1.7$ T. This clearly indicates type-II behavior with a large Ginzburg-Landau (GL) parameter κ . 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 $(-dB_{c2}/dT)_{T_{c0}} \cong B_{c2}' = 5.8$ 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

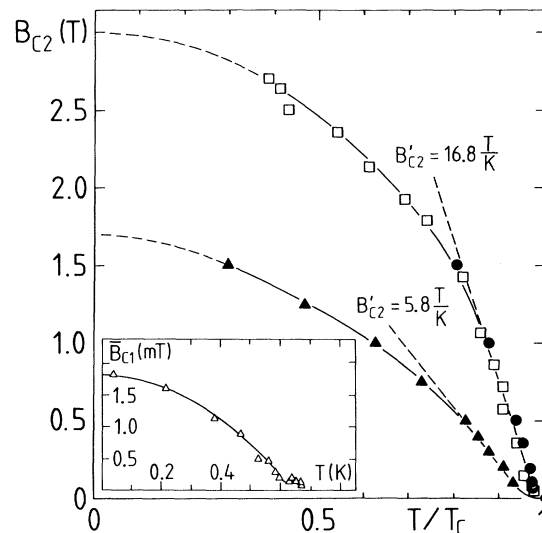


FIG. 2. Upper critical field, B_{c2} , of CeCu_2Si_2 as a function of the reduced temperature, T/T_c . While T_c is the transition temperature at $B_c = 0$ as measured, T_{c0} is defined by extrapolation of linear $B_{c2}(T)$ dependence to $B = 0$. Data were obtained from ac susceptibility (triangles: 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 \bar{B}_{c1} vs T (No. 7) as explained in the text.

by a mean Fermi wave number \bar{k}_F , yielding¹¹

$$B_{c2}' \cong \left(7.95 \times 10^{32} \frac{\text{T m}^2 \text{K}^2}{\text{J}^2} \right) \frac{\gamma T_c}{\bar{k}_F^4} + \left(4780 \frac{\text{T K m}^2}{\Omega \text{J}} \right) \gamma \rho_0. \quad (1)$$

Inserting into Eq. (1) measured⁷ data for T_c ($= 0.64$ K), the residual resistivity ρ_0 ($= 3.5 \times 10^{-8}$ Ω m), and the giant (heavy-fermion derived) coefficient γ ($\cong 2.0 \times 10^4$ J K⁻² m⁻³, with $V_{\text{mole}} \cong 5.03 \times 10^{-5}$ m³), we obtain $\bar{k}_F \cong 1.7 \times 10^{10}$ m⁻¹. Probably because of anisotropy effects, this is slightly larger than $\bar{k}_F \cong 1.6 \times 10^{10}$ m⁻¹ of the ordinary conduction-electron gas as previously estimated from the maximum high-temperature resistivity.¹² The latter \bar{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 con-

duction 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, $\bar{v}_F \simeq (6.02 \times 10^{-13} \text{ J K}^{-2} \text{ s}^{-1}) \bar{k}_F^2 \gamma^{-1} \simeq 8.7 \times 10^3 \text{ m s}^{-1}$, and their effective mass, $m^* = \hbar \bar{k}_F \bar{v}_F^{-1} \simeq 220 m_0$, 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., $\simeq 0.7 \times 10^{10} \text{ m}^{-1}$ (associated with $\bar{v}_F \simeq 1.5 \times 10^3 \text{ m s}^{-1}$ and $m^* \simeq 530 m_0$).

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 , ρ_0 and γ , we find the BCS coherence length $\xi_0 \simeq 1.9 \times 10^{-8} \text{ m}$. This is comparable to the mean free path of the quasiparticles, $l \simeq 1.2 \times 10^{-8} \text{ m}$. The London penetration depth (as $T \rightarrow 0$) assumes an unusually high value, i.e., $\lambda \simeq 2 \times 10^{-7} \text{ m}$. 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 κ 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 estimate¹ the "orbital critical field" (as $T \rightarrow 0$), i.e., $B_{c2}^*(0) \simeq 0.69 B_{c2}' \times T_c \simeq 2.6 \text{ T}$. 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 $T \rightarrow 0$) from (i) $B_{c2}^*(0)$ and (ii) the specific-heat coefficient γ [assuming a parabolic $B_{c2}(T)$ dependence]. We find almost the same values, namely (i) $B_{c2}^*(0) = B_{c2}^*(0)/\sqrt{2} \kappa_1(0) \simeq 66 \text{ mT}$ [with $\kappa_1(0) \simeq 1.26\kappa$ (Ref. 15)] and (ii) $B_{c2}^*(0) = [7.65 \times 10^{-4} (\text{m}^3/\text{J})^{1/2}] \gamma^{1/2} T_c \simeq 69 \text{ mT}$ (Ref. 16). This is much higher than $B_{c2}(0) \simeq 3 \text{ mT}$ of the conventional superconductor Cd with comparable T_c . Since $B_{c2}^*(0)$ 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 γ coefficient, in the former material.

With $B_{c2}^*(0)$ and κ we can also estimate the lower critical field through $B_{c1}(0) = B_{c2}^*(0) \ln \kappa_3(0) / \sqrt{2} \kappa_3(0) \simeq 6 \text{ mT}$, where $\kappa_3(0) = 1.15\kappa$ was used.¹⁵ $B_{c1}(0)$ agrees within an order of magnitude with the measured value ($\simeq 2.3 \text{ mT}$), 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 $\Delta C \simeq (6.86 \times 10^5 \text{ J T}^{-2} \text{ m}^{-3}) (2\kappa^2 - 1)^{-1} T_c B_{c2}'^2 \simeq 1.53 \times 10^4 \text{ J K}^{-1} \text{ m}^{-3}$, which is very close to the experimental value, $\Delta C = 1.59 \times 10^4 \text{ J K}^{-1} \text{ m}^{-3}$ (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 $\bar{k}_F = (1.6-1.7) \times 10^{10} \text{ m}^{-1}$, and they disprove, again, the picture of one $4f$ -derived heavy fermion per Ce ion¹⁴, for in this case $\bar{k}_F \simeq 0.7 \times 10^{10} \text{ m}^{-1}$ results in $\xi_0 \simeq 3 \times 10^{-9} \text{ m}$, $\lambda \simeq 3 \times 10^{-7} \text{ m}$, 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, $\rho_0 \leq 4 \times 10^{-7} \Omega \text{ m}$ (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 $B_{c2}' = (4.48 \times 10^3 \text{ T K m}^2 \text{ J}^{-1} \Omega^{-1}) \gamma \rho_0$, with $\gamma = 1.4 \times 10^4 \text{ J K}^{-2} \text{ m}^{-3}$ (Ref. 10), we estimate $B_{c2}' \leq 25 \text{ T/K}$. 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 ($\simeq 6 \text{ T/K}$) 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 $\simeq 17 \text{ T/K}$, 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 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 CeCu_2Si_2 , remains unknown.

One of us (F.S.) should like to acknowledge stimulating discussions with D. Rainer, R. A. Klemm, Ø. Fischer, E. Müller-Hartmann and P. Entel, and one of us (A.C.M.) with K. Kwasnitza and D. Wohlleben. This work was supported by Sonderforschungsbereiche 65 and 125 of the Deutsche Forschungsgemeinschaft.

^(a)Present address: Natuurkundig Laboratorium, Universiteit van Amsterdam, NL-1018 XE Amsterdam, The Netherlands.

^(b)Present address: Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland.

¹For a review, see Ø. Fischer, *Appl. Phys.* **16**, 1 (1978).

²See, e.g., A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, *Solid State Commun.* **17**, 27 (1975).

³D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, *J. Phys. (Paris), Lett.* **41**, L95 (1980).

⁴S. Horn, M. Loewenhaupt, E. Holland-Moritz,

F. Steglich, H. Scheuer, A. Benoit, and J. Flouquet, *Phys. Rev. B* **23**, 3171 (1981).

⁵F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, *Phys. Rev. Lett.* **43**, 1892 (1979).

⁶G. W. Hull, J. H. Wernick, T. H. Geballe, J. V. Waszczak, and J. E. Bernardini, *Phys. Rev. B* **24**, 6715 (1981).

⁷W. Lieke, U. Rauchschwalbe, C. D. Bredl, F. Steglich, J. Aarts, and F. R. de Boer, *J. Appl. Phys.* **53**, 2111 (1982).

⁸C. D. Bredl, H. Spille, U. Rauchschwalbe, W. Lieke, F. Steglich, G. Cordier, W. Assmus, M. Herrmann, and J. Aarts, in *Proceedings of the International Conference on Magnetism, Kyoto, 1982* (to be published).

⁹F. G. Aliev, N. B. Brandt, R. B. Wociev, V. V. Moshtaukov, and S. M. Chubinov, *Pis'ma Zh. Eksp. Teor. Fiz.* **35**, 435 (1982).

¹⁰F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, *J. Magn. Magn. Mater.* **15-18**, 889 (1980).

¹¹T. P. Orlando, E. J. McNiff, Jr., S. Foner, and M. R. Beasley, *Phys. Rev. B* **19**, 4545 (1979).

¹²W. Franz, A. Griessel, F. Steglich, and D. Wohlleben, *Z. Phys. B* **31**, 7 (1978).

¹³P. Nozières, *Theory of Interacting Fermi Systems* (Benjamin, New York, 1964).

¹⁴K. Andres, J. E. Graebner, and H. R. Ott, *Phys. Rev. Lett.* **35**, 1779 (1975).

¹⁵B. Serin, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2, p. 9.

¹⁶R. R. Hake, *Phys. Rev.* **158**, 356 (1966).

¹⁷Whereas $B_{c2}(T)$ of sample No. 4 was determined after annealing at 900 °C, the resistivity was measured in the unannealed state only and, therefore, can be taken only as an upper bound of ρ_0 for the annealed sample.

¹⁸From $B_{c2}' = 16.8$ T/K we would expect the residual resistivity of the (900 °C) annealed sample No. 4 to be $\rho_0 \approx 2.7 \times 10^{-7}$ Ω m, quite a reasonable value.

¹⁹See, e.g., M. Ikebe, K. Katagiri, N. Noto, and Y. Muto, *Physica (Utrecht)* **99B**, 209 (1980); P. Entel and M. Peter, *J. Low Temp. Phys.* **22**, 613 (1976).