Unusual B-T Phase Diagram of the Heavy-Fermion Superconductor $CeCu_2Si_2$

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Elastic constant and thermal expansion data for a high quality single crystal of $CeCu_2Si_2$ are presented. The data yield a detailed B-T phase diagram exhibiting a previously unknown high-field phase. From the unusual behavior of the elastic constants and the thermal expansion on entering the superconducting phase we deduce that, in contrast to other heavy-fermion superconductors, the superconducting phase of $CeCu_2Si_2$ does not coexist with the surrounding phase.

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Ever since the discovery of superconductivity in $CeCu_2Si_2$ [1], this heavy-fermion compound has played a central role in the physics of highly correlated electronic states. In this Letter we present experimental results which supply new details of the astonishingly rich B-T phase diagram, for instance, a formerly unknown phase in high magnetic fields (above 7 T, labeled B in Fig. 1). As in other heavy-fermion (HF) superconductors (among them UPt_3, URu_2Si_2, UPd_2Al_3), the superconducting (labeled sc) phase of $CeCu_2Si_2$ lies embedded in another phase (labeled A). Anomalies indicating the existence of phase A were first found in magnetoresistance [2] and nuclear magnetic resonance (NMR) [3] experiments. These experiments as well as muon spin rotation (μSR) [4] measurements showed that phase A does exhibit magnetic signatures, but whether of static [4] or dynamic [5] nature is still not clarified. In contrast to the above mentioned compounds, in the case of $CeCu_2Si_2$ we will argue that the superconductivity does not coexist with the enveloping phase A, but rather expells it homogeneously from the entire sample volume. This point of view resolves a long-standing problem with the sign of the elastic-constant changes on entering the sc state. From a careful analysis of the various phase transitions we can deduce electron-phonon coupling constants, the so-called Grüneisen parameters. In $CeCu_2Si_2$, both the normal and the sc Grüneisen parameters exhibit the typical heavy-fermion enhancement. Finally we can comment on the high pressure phases of $CeCu_2Si_2$ and we speculate on the physical origin of the various phases.

In the course of ac susceptibility, ultrasonic, and thermal-expansion measurements for a more precise determination of the A phase boundary [6–8], we faced two issues concerning crystal growth. One point was that the superconducting transition temperature T_c is very sensitive on copper stoichiometry [9]. It was found, however, that copper deficiency, caused by the high evaporation rate of copper from the melt, could be remedied by subsequent annealing in a saturated copper vapor atmosphere [10]. This procedure yielded single crystals with consistently high T_c's of 600–670 mK. It is remarkable that, at least at ambient pressure, T_c does not exceed T_A in any sample. The phases A and B were found to be much less sensitive on copper stoichiometry; the critical temperature of the A phase, $T_A \simeq 670$ mK, varies by no more than 10% in different samples with T_c's varying from 200 mK to 670 mK. A similar stability was observed for the B phase. An overall improvement in our sample quality is testified by the observation of de Haas-van Alphen oscillations both in the magnetization [11] and in the sound velocity [8].

The second point is that in some previously measured single crystals (for instance, samples No. 1 and No. 2 in [7]) the magnitude of the A-phase thermal expansion and ultrasound anomalies is so strongly reduced in fields below 5 T that our experiments could not resolve this part of the A-phase boundary in these samples. Up until now, we were unable to correlate the occurrence of this reduction with other properties like T_c. It is possible, however, to classify the different samples by means of their

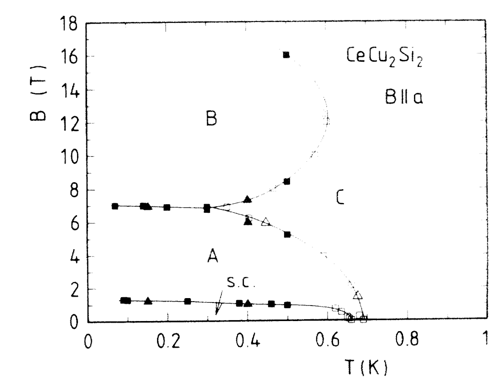

FIG. 1. B-T phase diagram of $CeCu_2Si_2$ for $B \| a$. Filled squares: Elastic constant anomalies at fixed temperature (Fig. 2). Open squares: Elastic constant anomalies at fixed field (Fig. 3). Filled triangles: Magnetostriction anomalies (not shown). Open triangles: Thermal-expansion anomalies in fixed field (Fig. 4).

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Grüneisen parameters; see below. The interference of superconductivity with another phase transition brings to mind the situation in some $A15$ compounds. V_3Si samples [12] are described which undergo a martensitic transition above T_c, as well as so-called nontransforming samples which nevertheless show strong precursor effects in elastic constants and thermal-expansion measurements (and even transform in a magnetic field greater than the critical field [13]). Since the term "nontransforming sample" would be misleading, we tag our $CeCu_2Si_2$ samples reduced anomaly (R) and nonreduced anomaly (NR). According to this nomenclature, samples No. 1 and No. 2 in Ref. [7] are R samples, whereas No. 3 and No. 4 are NR samples. In this paper we report mainly on an NR sample with $T_c = 670$ mK. As is shown in [14] for URu_2Si_2, the residual resistance can be estimated from the Alpher-Rubin effect and amounts to $\rho_0 = 5 \pm 1\ \mu\Omega$ cm for our NR sample, which is close to the lowest values reported in the literature [15]. The sample exhibits clear ultrasound and thermal-expansion anomalies for both the A and the sc transitions, which makes it ideal for studying the interaction between the A phase and superconductivity. The experiments were performed in dilution refrigerators with sc magnets and in a ^{3}He cryostat in the 25 T Helix magnet at the MPI-SNCI in Grenoble.

A typical isotherm for the c_{11} elastic mode as used to construct the phase diagram of Fig. 1 is shown in Fig. 2. A most disturbing feature of Fig. 2 is the fact that the elastic constant makes a large upward step on entering the superconducting phase. This is rather unusual and seemingly contradicts the common notion that superconductivity is a symmetry breaking transition (breaking gauge symmetry in normal BCS superconductivity and possibly additional symmetries in unconventional superconductors like UPt_3). This can be seen from Ginzburg-Landau types of considerations where the change of an elastic constant c_{ii} on going from a more symmetric to a less symmetric phase is always negative. For a superconducting transition, for instance, the change is given (in the hydrodynamic limit) by [16]

$$\Delta c_{ii} = -(\Omega_i^{sc})^2 T_c \Delta C_p \,. \qquad (1)$$

Here $\Omega_i^{sc} = -(1/T_c)(\partial T_c/\partial \epsilon_i)$ is the superconducting uniaxial Grüneisen parameter for the strains ϵ_a and ϵ_c and ΔC_p is the specific-heat jump per unit volume at the transition temperature T_c. For the case that a lower temperature (field) phase is of higher symmetry, the change in the elastic constant can be positive on lowering the temperature (field). As examples, see the low-temperature orthorhombic-tetragonal structural phase transition in the organic compound MAMC [17] and for $CeCu_2Si_2$ the low-field B-C transition of the c_{11} mode at $B = 8$ T and $T = 0.5$ K in Fig. 2.

Applying this kind of reasoning to the A-sc transition, a net upward jump in the elastic constants on entering the superconducting phase is possible if a negative superconducting step is counteracted by a (larger) positive step due to a simultaneous change of the A order parameter back to zero. This is tantamount to the conclusion that the A phase and the sc phase exclude each other and do not coexist. Further support for this point of view can be found in Figs. 3 and 4. In Fig. 3 the c_{11} mode is plotted as a function of temperature for different magnetic fields for the NR sample with nearly coinciding T_A and T_c. It is clearly seen that the elastic anomaly at T_A is partly suppressed in zero field due to the onset of superconductivity. The anomaly at T_c can only develop fully in a field $B > 1$ T when the separation between T_A and T_c has become large enough. The same behavior can be seen in other modes, for instance, in the transverse c_{66} mode as shown in Fig. 5 of Ref. [7]. The inset of Fig. 4 shows the analogous development of the a-axis thermal-expansion coefficient. The specific-heat anomaly accompanied by the crossing of the A-phase boundary becomes most clear in samples with strongly reduced T_c values [see, e.g., Fig. 7(a) of Ref. [7]]. Although the A-phase anomalies in the R samples are much less clear, these samples show qualitatively the same behavior of sharply increasing elastic constants on entering the sc phase (not shown).

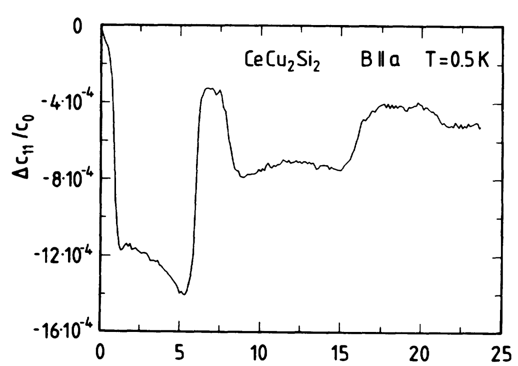

FIG. 2. Relative change of the elastic constant c_{11} of a $CeCu_2Si_2$ NR crystal as a function of magnetic field at $T = 0.5$ K and $B \| a$.

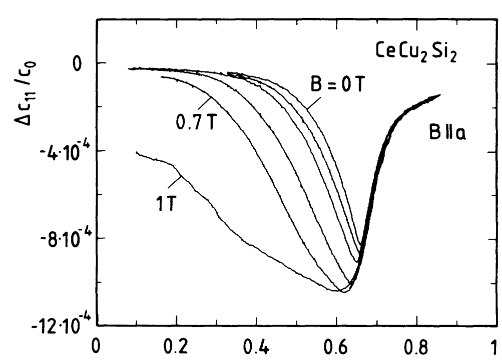

FIG. 3. Relative change of the elastic constant c_{11} of the $CeCu_2Si_2$ NR crystal as a function of temperature in magnetic fields $0 < B < 1$ T with $B \| a$. Unmarked curves represent measurements at 0.1, 0.2, and 0.4 T.

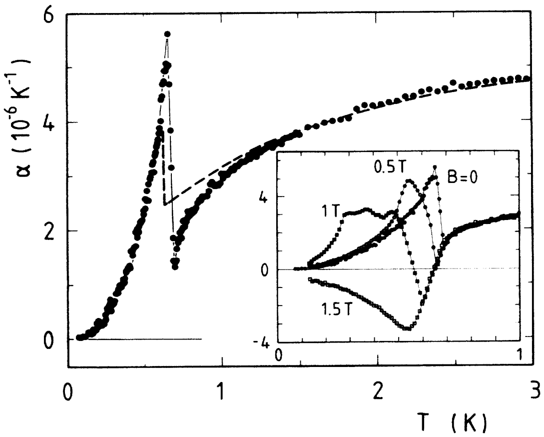

FIG. 4. Coefficient of thermal expansion along the a axis of an NR-type $CeCu_2Si_2$ sample (●) and of an R-type sample (---) [7] in zero magnetic field. Inset: a axis thermal-expansion coefficient of the NR-type sample in different magnetic fields with $B \| a$.

Assuming simple additivity of the elastic-constant changes associated with the appearance and disappearance, respectively, of the order parameters of the sc and the A phases, one can extract these changes from our measurements. Unfortunately, due to the background slope of the elastic constants as a function of field or temperature, one cannot evaluate the small C-sc step heights from Fig. 2 or Fig. 3 as the difference of high temperature (field) and low temperature (field) values of c_{11}. From Fig. 3 one obtains a relative change in c_{11} for the C-A transition of about -1×10^{-3} (full height of the anomaly at $B=0.7$ T). For the A-sc transition one gets $+8\times10^{-4}$ (full height of the zero-field anomaly in Fig. 3). This leaves about -2×10^{-4} for the total c_{11} change from the paramagnetic C phase to the sc phase (i.e., the vertical difference between the minima of the zero field and the 0.7 T curves). This result is in agreement with a more elaborate analysis of the different step heights involving closed loops in the B-T plane, which yields values between -1×10^{-4} and -2.2×10^{-4} for the C-sc step in samples with different T_c's [18]. Despite sample to sample variations, these values are characteristic of a heavy-fermion superconductor, with respect to both the sign and the magnitude.

A similar procedure can be used to extract the corresponding anomalies in the a axis thermal-expansion coefficient α_a, which is shown in Fig. 4. Especially from the inset of Fig. 4 it is clear that also $\alpha_a(T)$ is composed of two contributions, namely a sharp positive jump due to superconductivity and a decrease just above T_c due to the incipient C-A transition. The full C-A transition alone shows up in an overcritical field of $B=1.5$ T and amounts to $\Delta\alpha_a^{C\text{-}A}\simeq -6\times10^{-6}\ \mathrm{K}^{-1}$; see inset of Fig. 4.

In order to extract the sc step in zero field we compare the data with those of an R-type crystal [7]; cf. main panel of Fig. 4. We find perfect coincidence for temperatures above and below T_c. Following our analysis for the elastic constants we ascribe the difference in α_a just above T_c to the influence of the A phase. For the sc transition alone we get $\Delta\alpha_a^{sc}=+(2.9\pm0.5)\times10^{-6}\ \mathrm{K}^{-1}$. A similar procedure for α_c (not shown) yields $\Delta\alpha_c^{sc}=-(2.1\pm0.5)\times10^{-6}\ \mathrm{K}^{-1}$.

TABLE I. Absolute elastic constants of $CeCu_2Si_2$. The elastic constants were determined at 4.2 K, except c_B [20] and c_{13} which were computed from $c_B=[2(c_{11}+c_{12})+c_{33}+4c_{13}]/9$. The error in c_{11}, c_{12}, c_{33}, c_{44}, and c_{66} is 5%; in c_B and c_{13} 20%.

c_{ij}	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	c_{66}	c_B
10^{11} erg/cm^3	17.1	15.2	5.2	13.8	4.7	2.2	11.0

Now we proceed to determine the electron-phonon coupling constants, i.e., the Grüneisen parameters for the normal and the sc state. The necessary elastic-constant values are listed in Table I. The absolute value of the normal-state Grüneisen parameter $|\Omega_a^n|$ we determined from elastic-constant and specific-heat measurements in the temperature range between 5 K and T_c [19]. The absolute value of the superconducting Grüneisen parameter $|\Omega_a^{sc}|$ is computed with the help of Eq. (1), with $\Delta c_{11}/c_{11}=-(2\pm0.5)\times10^{-4}$, $\Delta C_p=(1.4\pm0.5)\times10^5$ erg/cm^{3}K [7] and $T_c=0.67$ K; see Table II. We can compare these values with results gained from thermodynamically equivalent relations which include thermal-expansion coefficients and are given in Eq. (2) [14]:

$$\Omega_a^{sc}=[(c_{11}+c_{12})\Delta\alpha_a+c_{13}\Delta\alpha_c]/\Delta C_p\,,$$
$$\Omega_c^{sc}=(2c_{13}\Delta\alpha_a+c_{33}\Delta\alpha_c)/\Delta C_p\,. \quad (2)$$

Here $\Delta\alpha_{a,c}$ are changes at T_c of the thermal-expansion coefficients parallel and perpendicular, respectively, to the tetragonal basal plane, c_{ij} are elastic constants, and ΔC_p is the specific-heat jump at T_c. Note that we get an analogous expression valid for the normal-state Grüneisen parameters if we use absolute values of $\alpha_{a,c}$ and C_p instead of differences in Eq. (2). Using these expressions and the specific heat from [7], we calculated the normal-state Grüneisen parameters at $T=1$ K. Together with the sc Grüneisen parameters computed from Eq. (2) they

TABLE II. Normal (at $T=1$ K) and superconducting Grüneisen parameters of $CeCu_2Si_2$ R and NR samples (see text). The absolute uncertainty is ±10; the comparative error is smaller. All samples have their T_c in the range 620–670 mK.

	Ω_a^n	Ω_c^n	Ω_v^n	Ω_a^{sc}	Ω_c^{sc}	Ω_v^{sc}
From c_{ii},C_p [19] and Eq. (1) NR type	|75|			|64|		
From α_i,C_p,c_{ii} Eq. (2) NR type	69	32	55	60	1	35
R type	68	30	54	31	−15	10

are listed in Table II. For comparison, we listed the Grüneisen parameters for the R samples No. 1 and No. 2 of [7]. The normal-state Grüneisen parameters are virtually identical for R and NR samples. The sc Grüneisen parameters on the other hand are significantly reduced for the R samples as compared with the NR sample. Note that for $CeCu_2Si_2$ Ω_v^{sc} and Ω_v^n have the same sign, in contrast to UPt_3 (Ref. [16]) and URu_2Si_2 (Ref. [14]) where the two have the same magnitude, but opposite signs.

As a next topic we comment on the pressure dependence of T_c. Specific-heat measurements under pressure have been performed up to 1 kbar [21] and susceptibility experiments up to 80 kbar [22]. Neither experiment observes the A-phase boundary explicitly. The volume Grüneisen parameters as determined from these experiments are $\Omega_v^{sc}=7$ [21] and $\Omega_v^{sc}=4$ [22]. Extrapolation of the high-pressure $T_c(p)$ curve [22] towards zero pressure gives an $\Omega_v^{sc}=-7$ (with an extrapolated zero pressure $T_c=2.8$ K). All these Ω values are smaller than our Ω^{sc} for the NR sample listed in Table II. This probably reflects the fact that one has to take into account the interplay between superconductivity and phase A. Unfortunately, it is not clear whether the samples used in these experiments are of R or NR type. Nevertheless it would be interesting to follow and analyze the pressure dependence of the various phases.

Finally we speculate on the origin of the different phases. At first sight, the A and B branches of the B-T phase diagram suggests an AF-SDW with strong uniaxial anisotropy leading to a spin-flop-like transition on going from A to B. However, the magnetic response of the system is very weak. ac susceptibility anomalies at the phase boundaries are very small whereas elastic-constant and thermal-expansion changes in NR crystals are very distinct. Preliminary neutron scattering experiments did not reveal any superstructure as indication for a commensurate spin-density wave (SDW) or charge-density wave (CDW) order parameter for the A phase. However, there exists a more general possibility. Analogously to the case of unconventional superconductivity, a density-type (CDW, SDW) order parameter can have an unconventional counterpart belonging to a nontrivial representation of the relevant crystal group. Such an order parameter will have little magnetic reponse and will not lead to additional Bragg peaks. The symmetry classification has been discussed by Gor'kov and Sokol [23]. In a simple perfect nesting model with nesting vector Q one can indeed predict the observed A phase expulsion for suitable representations of both order parameters [24]. If Q is a zone boundary vector, one has an antiferroquadrupolar state with itinerant quadrupole moments. Another possible mechanism for the A-phase transition is proposed by [25] and depends on a topological change of the heavy quasiparticle bands in an external magnetic field.

The expulsion of the A phase in this picture is only possible when T_c is not too far below T_A, since otherwise the condensation energy corresponding to the order parameter of the A phase is already too large to be suppressed by the onset of superconductivity. This seems indeed to be the case for samples with $T_c \simeq 0.2 T_A$. In these samples the elastic-constant step at T_c is downward, indicating that no expulsion of the A phase but rather coexistence with superconductivity takes place. This case may be similar to URu_2Si_2 where one has a Néel temperature $T_N \simeq 18$ K and a much lower $T_c \simeq 1$ K. The URu_2Si_2 coexistence of both phases is observed as seen again from the downward step in the elastic constants at T_c [14].

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