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Observation of a high-field anomaly in the low-temperature specific heat of $CeCu_2Si_2$

B. Andraka
Department of Physics, University of Florida, Gainesville, Florida 32611

G. R. Stewart
Department of Physics, University of Florida, Gainesville, Florida 32611
and University of Augsburg, Augsburg, Germany

F. Steglich
Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

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We have performed high-magnetic-field, to 16 T, low-temperature specific-heat measurements for $CeCu_{2.2}Si_2$, $CeCu_2Si_2$, and $CeCu_{1.9}Si_2$. The first two materials, which are superconducting, exhibit a pronounced structure in C/T at $T \sim 0.6$ K and $H \geq 10$ T. Changing the field from 10 to 16 T does not affect the anomaly. The nonsuperconducting, $CeCu_{1.9}Si_2$, sample does not exhibit a similar anomaly in the investigated temperature range, 0.32–1 K. Possible correlations between this structure and the low-temperature, high-field phase diagram of $CeCu_2Si_2$ are discussed.

The discovery[1] of superconductivity in $CeCu_2Si_2$ gave birth to the dynamically developing field of heavy-fermion superconductivity.[2] However, despite this favorable status of $CeCu_2Si_2$ among all other heavy-fermion materials and despite more than a decade of research, our understanding of its low-temperature state and superconductivity is still unsatisfactory.

$CeCu_2Si_2$ is an extremely fascinating material for the multitude of phenomena it exhibits at low temperatures, below 1 K. Beside the mentioned superconductivity, $CeCu_2Si_2$ undergoes a small moment antiferromagnetic ordering (~ 0.6 K) seen in microscopic measurements, Cu NMR (Ref. 3) and μSR.[4] The specific heat divided by temperature (C/T) versus temperature reveals a broad but clearly visible maximum[5] at $T \sim 0.4$ K at magnetic fields which are overcritical for superconductivity. This structure, however, is generally ascribed[5,6] to another type of cooperative phenomenon, a coherence effect in a Kondo lattice. According to theoretical predictions,[6] translational symmetry of Kondo centers leads to a partial gapping of the Kondo resonance states at E_F. The formed pseudogap is an order of magnitude smaller than the single-ion temperature scale, the Kondo temperature, T_K.

Several experimental observations corroborate the coherence gap interpretation. First of all, the temperature corresponding to the C/T maximum, T_M, is about 20–30 times smaller than T_K; $T_K \sim 10$–15 K as calculated from the specific heat.[5] Secondly, breaking up the lattice periodicity by substituting small amounts of La or Y for Ce reduces T_M and smears the anomaly.[5] Finally, this structure has the predicted magnetic-field dependence for small fields of the order of 1 T. Such fields broaden the anomaly and move it to lower temperatures.[5,7] However, the existence[5] of the broad C/T maximum at relatively high temperature of 0.4 K for the highest field previously applied, 8 T in some samples, is somewhat inconsistent with the above interpretation. The 8-T field corresponds to a temperature of about 9 K, assuming $\mu_{\text{eff}} = 1.65\mu_B$ as measured by neutron scattering[8] at 10 K. The existence of the coherence gap is not anticipated for fields greater or equal to T_K.[9] However, high-field magnetization measurements reveal that $M(H)$ is linear up to at least 50 T, where its value corresponds to only $1\mu_B$/Ce.[10] These observations necessitate further studies of $CeCu_2Si_2$ at higher magnetic fields.

Here, we report low-temperature specific-heat studies at magnetic fields to 16 T. In addition we have attempted to seek correlations between the C/T structure and superconductivity.

One of the puzzling characteristics of $CeCu_2Si_2$ is the unusually strong interdependence between superconductivity and Cu stoichiometry.[5,7,11] Superstoichiometric Cu stabilizes the superconducting state. Samples which vary in nominal composition from $CeCu_2Si_2$ to $CeCu_3Si_2$ can be superconducting with $T_c > 0.5$ K while slightly Cu deficient samples are not superconducting. ($CeCu_{1.9}Si_2$ in our study is not superconducting above 50 mK.) This property was utilized by us to control superconductivity in the investigated material. The samples studied were corresponding to the following nominal stoichiometries: $CeCu_{1.9}Si_2$, $CeCu_2Si_2$, and $CeCu_{2.2}Si_2$. The typical size of the specific-heat sample was 0.5 mg. The homogeneity of $CeCu_2Si_2$ and $CeCu_{2.2}Si_2$ was investigated by performing measurements on two different pieces cut out from different parts of the same mother sample. The studied samples were additionally characterized via an ac magnetic susceptibility technique.

In agreement with previous reports,[5,7] no diamagnetic shielding was detected for $CeCu_{1.9}Si_2$ above 0.32 K, while according to the ac susceptibility, $CeCu_2Si_2$ and $CeCu_{2.2}Si_2$ samples were superconducting below 0.63 and

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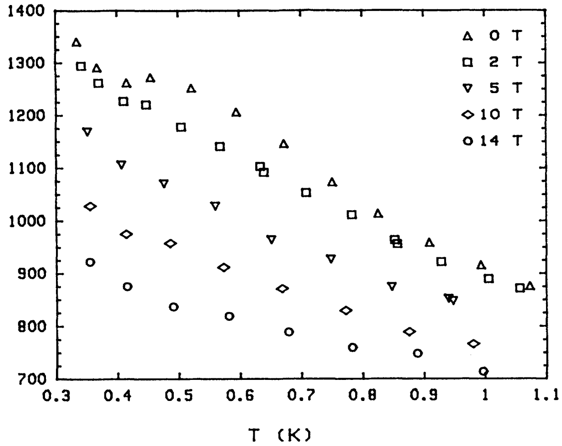

FIG. 2. C/T vs T for $CeCu_{1.9}Si_2$. The absolute error of temperature measurement is smaller than 20 mK for all fields. The absolute error of the specific-heat values, as determined from measurements of high-purity Au samples obtained from NBS, is smaller than 5% at $H=0$ and smaller than 10% at 16 T.

0.65 K, respectively (Fig. 1). Both investigated pieces of $CeCu_{2.2}Si_2$ showed similar sharp transitions into the superconducting state. The two $CeCu_2Si_2$ samples [denoted as $CeCu_2Si_2$-*A* and $CeCu_2Si_2$-*B* in Figs. 1(a) and 1(b), respectively], on the other hand, have broad incomplete transitions. Moreover, the ac susceptibility results indicate a large degree of inhomogeneity in the $CeCu_2Si_2$ material. Some systematic differences between $CeCu_2Si_2$-*A* and $CeCu_2Si_2$-*B* samples were also observed in the specific-heat measurements discussed next.

The magnetic-field dependence of C/T for the Cu-deficient sample is presented in Fig. 2. Except for a small shoulder at about 0.5 K for zero field, the C/T data do not exhibit any structure in the investigated temperature range for the fields applied. The low-temperature C/T decreases monotonically with an increase of T and H, in agreement with trends observed for other Ce-based heavy fermions and in qualitative agreement with the standard single-impurity model.[12]

The specific heat of the stoichiometric $CeCu_2Si_2$ samples is anomalous in several respects. We discuss results for the two $CeCu_2Si_2$ samples, *A* and *B*, separately. The zero-field C/T data for $CeCu_2Si_2$-*A* (Fig. 3) have a pronounced maximum at about 0.62 K. It is, however, unlikely that this maximum is entirely due to the superconducting transition. The ac susceptibility data indicate an onset of a broad transition at about 0.63 K. Therefore, one would expect a peak in C/T, which represents bulk superconductivity, at a somewhat lower temperature. Moreover, the 2-T C/T vs T curve, see Fig. 3, has a similar shape to the 0-T curve. The 2-T shift of the C/T maximum is less than 0.05 K, which is too small[5,7] to be associated with the decrease of T_c. Both the 0- and 2-T structures must therefore correspond to some other phenomenon. The next field applied, 5 T, broadens considerably the anomaly, such that only a shallow maximum (see Fig. 3) can be detected near 0.4 K. There is no peak in C/T in the investigated temperature range for the still higher field of 7 T. The results discussed so far are essentially in agreement with previous studies.[5,7] An observation made by us is the structure, see Fig. 3, in C/T for the highest field applied, 14 T. C/T has a clearly visible maximum at about 0.58 K.

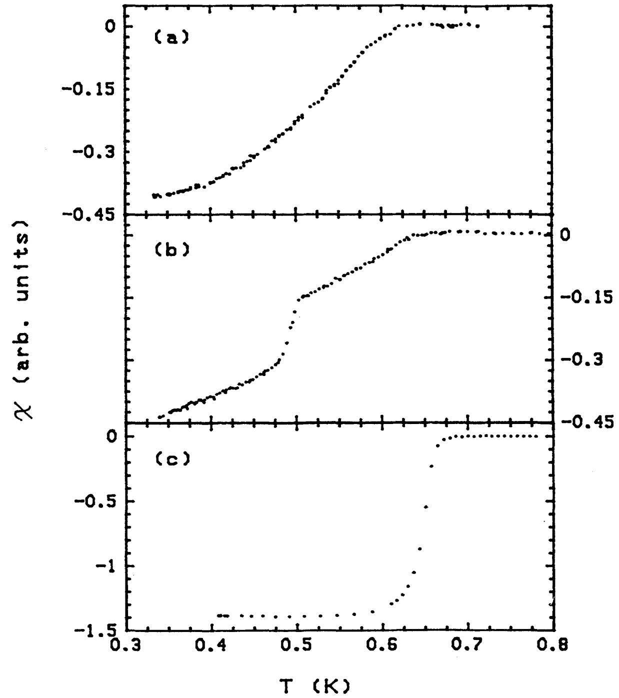

FIG. 1. Zero-field ac susceptibility for (a) $CeCu_2Si_2$-*A*, (b) $CeCu_2Si_2$-*B*, (c) $CeCu_{2.2}Si_2$; $f=86$ Hz.

A somewhat similar magnetic-field dependence of the specific heat was measured for the second $CeCu_2Si_2$ sample (No. *B*; see Fig. 4). The shoulder seen for $H=0$ at temperatures lower than 0.5 K is probably related to superconductivity as implied by both ac susceptibility and

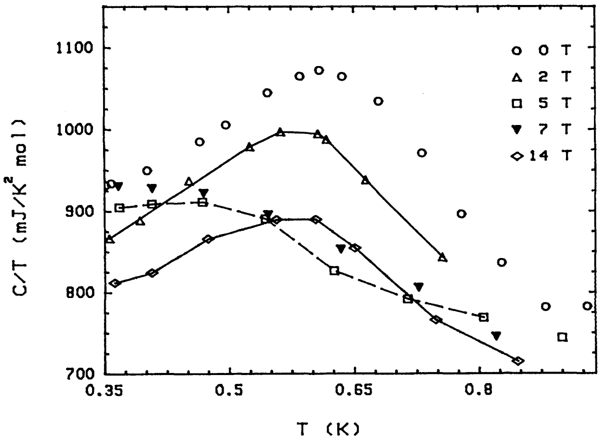

FIG. 3. C/T vs T for $CeCu_2Si_2$-*A*. Lines drawn are to aid the eye.

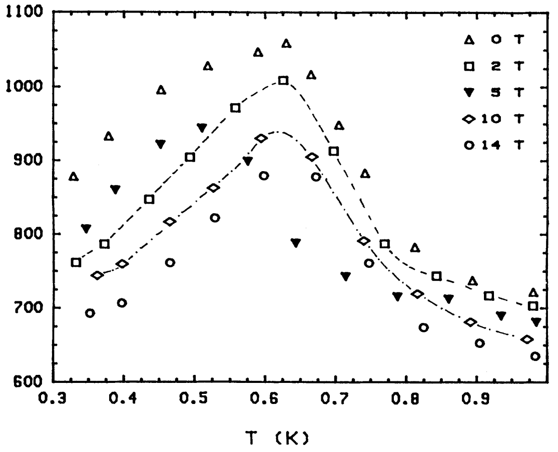

FIG. 4. C/T vs T for $CeCu_2Si_2$-B.

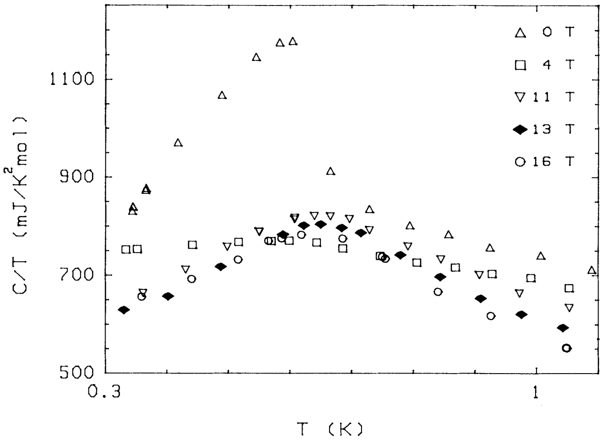

FIG. 5. C/T vs T for $CeCu_{2.2}Si_2$.

the 2-T specific-heat results. The 2-T field leaves the main peak in C/T at about 0.63 K essentially unaffected but removes the shoulder. The field of 5 T shifts the maximum to lower temperatures by about 0.1 K although leaves it still relatively sharp in contrast to the A sample for which only a very broad anomaly is seen at lower temperatures. Finally, a well-pronounced peak in C/T appears for $H = 10$ T at ~ 0.62 K and stays at about the same temperature for $H = 14$ T.

The two superstoichiometric $CeCu_{2.2}Si_2$ samples had almost identical ac susceptibility and specific-heat results and therefore only one of them is discussed (Fig. 5). $CeCu_{2.2}Si_2$ is clearly a bulk superconductor; the zero-field C/T reaches 1200 mJ/K^2 mol at about 0.6 K. The effect of small fields is, in agreement with previous results,[5,7] analogous to the case of stoichiometric samples. A relatively broad and shallow maximum in C/T is observed at about 0.5 K. The C/T data for the high fields of 11, 13, and 16 T feature sharp peaks at about 0.65 K. It is important to note that an increase of the field from 11 to 16 T affects neither the shape nor the temperature of the anomaly (T_h) in any significant manner, similar to our results for stoichiometric $CeCu_2Si_2$. The Cu nuclear contribution to the specific heat has not been subtracted from any of the data sets presented. Such a subtraction (about 10% of the total C at 0.32 K and 16 T) would only result in further visual enhancement of the anomaly.

Summarizing, our low-field measurements (≤ 7 T) confirm previous reports on $CeCu_2Si_2$. The low-field C/T anomaly is consistent with either a coherence gap[5,7] or a long-range antiferromagnetism interpretation.[13] We would like to point to a possible correlation between the occurrence of this anomaly and Cu stoichiometry and superconductivity. Cu deficient samples, which are not superconducting, do not exhibit a peak in the low-field C/T above 0.32 K.[5,7] This correlation is corroborated by investigations on superconducting and nonsuperconducting samples of $Ce_{1-x}M_xCu_2Si_2$, where M are other metallic elements like La, Y,[14,15] or Th.[16,17] We note that occurrence of this anomaly in close vicinity to T_c has a consequence for the accurate determination of the $\Delta C/T_c$ ratio, measuring the coupling strength.

These high-field (>8 T) measurements of the low-temperature specific heat for $CeCu_2Si_2$ reveal the existence of structure in C/T in superconducting (stoichiometric or Cu-rich) samples at about 0.6–0.65 K. Occurrence of this anomaly for the same samples which exhibit the lower field structure, at $T_l(H)$, seems to imply that they correspond to the same phenomenon. However, persistence of the anomaly in magnetic fields as high as 16 T (actually the anomaly is most pronounced at high fields) is inconsistent with both magnetic transition and coherence effects interpretations of the low-field structure. Moreover, such an assumption would imply nonmonotonic field dependence of $T_h(H)$. In fact, another phase transition line, $T_h(H)$, separating from $T_l(H)$ in a tricritical point near 6–7 T has been recently discovered through elastic constants and thermal expansion measurements.[17]

The insensitivity of T_h to magnetic fields greater than 10 T suggests the possibility of a field-induced structural transition, which was also suggested as a possible source of the low-field transition at $T_l(H)$.[18] The superconductivity of $CeCu_2Si_2$ may then be related to the closeness of the stoichiometric and Cu-rich samples to structural instabilities as it was postulated in Ref. 19. The fact that $CeCu_2Si_2$ is the only known Ce-based heavy fermion which becomes a superconductor at low temperatures may be considered consistent with this speculation.

Finally, we could not detect any signatures of the low-temperature anomalies via ac susceptibility and electrical resistivity measurements. However, the size and shape of the samples for which the heat-capacity measurements were performed were not optimal for our ac susceptibility and electrical resistivity measurements.

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