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More evidence for magnetic ordering in $CeCu_6$ at mK temperatures

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dc-magnetization measurements in various magnetic fields on two samples from the same single crystal of $CeCu_6$ in a superconducting quantum interference device system show a plateau of the magnetic susceptibility between 400 and 50 mK, followed by a Curie-like increase towards lower temperatures. At very low temperatures the magnetization starts deviating from a $1/T$ behavior, saturating around 900 μK in 2.7 mT, the highest B/T ratio obtained in this experiment. We show that this Brillouin behavior must be due to a tiny amount of the magnetic ion Gd^{3+}, present in a concentration of 1.5(3) ppm. After subtracting this contribution from the magnetization curves in various lower fields, a field-dependent structure with a drop of the magnetic susceptibility around 3 mK is left. This decrease is reduced with increasing field and has vanished in 2.7 mT. In the lowest fields the structure is very similar to one observed in ac-susceptibility measurements. The fact that this drop of χ occurs in different samples and that it can be quenched by the magnetic field points to an intrinsic antiferromagnetic ordering in $CeCu_6$ around 3 mK. We cooled one sample to a lowest temperature of 450^{+40}_{-10} μK in a field of 0.3 mT. The susceptibility further decreases with decreasing temperature and shows a small shoulder at 650 μK. In addition, we measured the specific-heat capacity of the same single crystal of $CeCu_6$ in zero magnetic field down to a temperature of 11 mK. Between 40 and 11 mK c/T increases from 1.55 to 2.8 J/mole K^2, most likely an indication of the high-temperature end of the magnetic transition.

INTRODUCTION

Most of the heavy fermion compounds order either magnetically or superconductively at temperatures above 20 mK, often with simultaneous existence of the two ordered phases. The ground state of a given system is determined by an interplay of Ruderman-Kittel-Kasuya-Yosida (RKKY) and Kondo interactions, which depends on many parameters: the exchange coupling between the f moments and the conduction-band electrons, the electronic configuration and symmetry of the ligands, and the occurrence of correlations. In the case of heavy fermion superconductors the mechanism for Cooper pairing has to be considered in addition. It is believed to be unconventional at least in UPt_3. If the RKKY interaction is dominant, magnetic ordering occurs prior to Kondo screening. In the other case the f electrons get strongly hybridized with the conduction-band electrons and become itinerant. Through the spatial extension of the Kondo screening, parameters like the crystal quality (e.g., level of impurities), amount of local strain, or superstructure also play an important role. If superconductivity would be mediated through magnetic interactions, this would also depend on local structure parameters.

$CeCu_6$ is known to be intermediate between localized-state and itinerant behavior. It has an extremely high γ ($\approx$1600 mJ/mole K^2) and it exhibits strong magnetic correlations[1] as well as antiferromagnetic order setting in with only 1.3% of doping with Ag or Au (i.e., with a slightly negative chemical pressure).[2,3] Therefore it is astonishing that it belongs to the few systems that do not order down to 20 mK (together with, e.g., polycrystalline $CeAl_3$, CePtSi, and $UAuPt_4$).

Polycrystalline $CeAl_3$ has been cooled to 800 μK by Avenel *et al.*[4] and no ordering was observed. There were reports, however, that single-crystalline $CeAl_3$ orders antiferromagnetically around 1 K.[5] It was argued that in this case a more uniform strain in the single crystal would favor the magnetic interaction while it might be suppressed in the polycrystal. Since we obtained a high-quality single crystal of $CeCu_6$ we decided to measure its static magnetic susceptibility down to the lowest possible temperatures (we obtained 450 μK). During the course of our experiment we learned about similar activities of Jin *et al.* and of their results presented at the LT-20 meeting with peaks around 3 mK and 500 μK for the magnetic ac susceptibility in low magnetic fields.[6] In addition to the magnetic measurements we determined the specific-heat capacity of the same single crystal of $CeCu_6$ down to 11 mK, considerably lower than in previous experiments.[1,7–9]

EXPERIMENT

The static magnetic susceptibility was measured in a superconducting quantum interference device (SQUID) magnetometer[10] in which the residual magnetic fields (earth field, cryostat after demagnetization) could be compensated in the z direction to a level of about 0.01 mT ($B_{\text{total}} \approx 0.05$ mT). The cooling was provided by a nuclear demagnetization state ($PrNi_5$) with a final temperature between 420 and 700 μK, depending on the final field after the demagnetization. This temperature, as well as all temperatures during the cycle of the nuclear stage, were determined by pulsed NMR on Pt wires and on bulk Cu with both samples located in the center of the 6 T magnet used for demagnetization. The two temperatures agreed to within 5% at the lowest temperatures. All the samples used in this work came from the same large single crystal grown by Bucher, Konstanz, with the Czochralski method. The cerium, of 99.99% quality, was provided by Johnson-Matthey with a stated purity of 30 ppm for La, Pr, and Nd combined, the rest being Al, Si, Ca, O, N, and

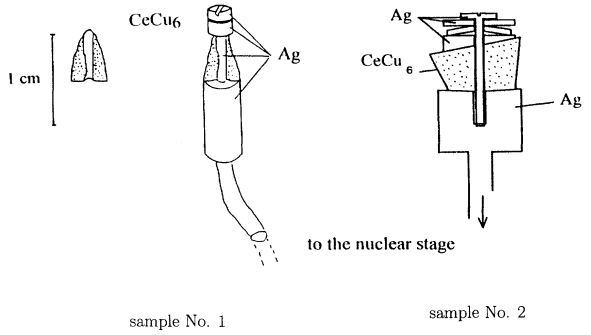

FIG. 1. Sketch of the $CeCu_6$ samples used in this work and their thermal connection to the nuclear stage.

H. The single-crystalline quality and the crystal orientation were determined by x-ray structure analysis. The lattice parameters $a=8.0883(64)$, $b=5.0794(20)$, and $c=10.1218(34)$ agree very well with literature data.[11]

The crystal had a short cylindrical shape with a narrow cone at one end from the beginning of the growth. This end was cut off by spark erosion and cut into two pieces; both had a hole through the center also made by spark erosion. During this procedure the very end broke apart, leaving a little more than a half-cone (sample 1, largest diameter ~3.5 mm, height 2.5 mm). The second sample was in the shape of a conical cylinder of about 4 mm diam and 2.5 mm height (see Fig. 1). These two pieces were each screwed to a Ag rod with a $5N$ Ag screw after the surface was etched with acetic acid and the contact area was gently polished with corundum powder. The squeezing force is hard to estimate; it should have been of the order of 1 N. The magnetic properties of the Ag holder were checked separately; it was found to be less than 2% of the signal from either sample. The same was the case for the Ag paint (DuPont) applied in the case of the second sample in addition to the squeeze contact after the sample had been screwed on.

In both cases the thermal conductance was determined independently at temperatures above 11 mK from thermal time constants and the known heat capacity of the samples (see below). Since the conductance scaled with T, this behavior was extrapolated to lower temperatures. The temperature of the samples was then calculated from the $PrNi_5$ temperature, the conductance of the thermal contact, and the external heat leak estimated from thermal gradients around 1 mK. The latter was assumed to be independent of temperature.

The measurements of the specific-heat capacity were performed on the large remaining part of the crystal (1.9 g) with a diameter of about 8.5 mm. We used both the usual semiadiabatic heat-pulse technique and the adiabatic warm-up method with a superconducting heat switch described in more detail elsewhere.[12] The sample was clamped with a cylindrical Ag ring of $5N$ purity whose contribution was found to be negligible.

RESULTS

The specific-heat capacity of $CeCu_6$ is shown in Fig. 2. The open squares indicate data taken with the semiadiabatic heat pulse technique; the open circles indicate data taken from the warm-up method. Both agree very well even below 20 mK. The data show a distinct deviation from the constant γ_n below 40 mK with c/T rising from 1.55 to 2.8 J/mole K^2 at 11 mK.

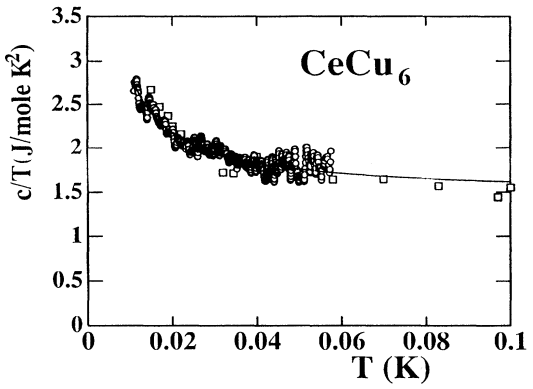

FIG. 2. Specific-heat capacity of a single crystal of $CeCu_6$ in zero magnetic field. ○: data taken with the adiabatic warming method; □: data from the semiadiabatic heat pulse technique. The solid line is a guide to the eye.

Susceptibility data from the first sample of $CeCu_6$ in magnetic fields from 0.01 to 1.39 mT, applied in the z direction, were taken down to slightly less than 1 mK. The values of χ were calibrated against the signal from a superconducting sample and commonly connected to an absolute value at 600 mK taken from a different experiment.[13] Between 30 mK and 1 K (our highest temperature) they all agree to within 0.6%; only the curve in the lowest field shows an additional variation (of unknown origin) around 600 mK. The well-known Curie-Weiss law from room temperature downward[2,13] is followed by a plateau between 400 and 50 mK (see Fig. 3) which can be attributed to the onset of a coherent heavy fermion state. At lower temperatures, this plateau is again followed by a Curie-like increase with a slight signature of saturation at the highest B/T value (0.81 mT, 800 μK) reached in the first experiment when the final field at the nuclear stage was 68 mT. In the curves of Fig. 3

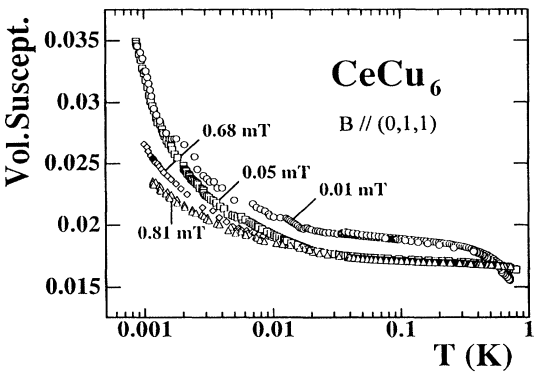

FIG. 3. dc-magnetic susceptibility of a single crystal of $CeCu_6$ (sample 1) after subtraction of the nuclear susceptibility of Cu. The different fields, 0.01 to 0.81 mT, were oriented along the (0,1,1) crystallographic direction. The impurity contribution has not been subtracted yet.

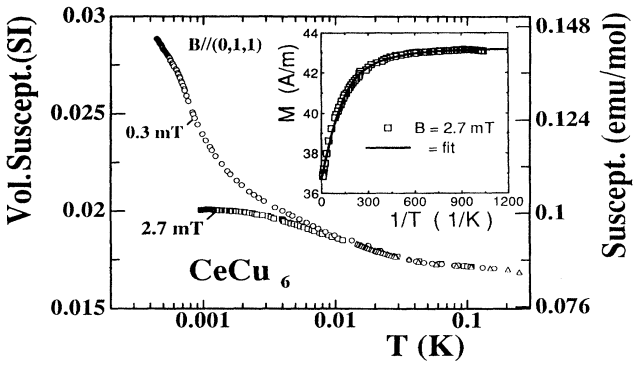

FIG. 4. Static magnetic susceptibility of a single crystal of $CeCu_6$ (sample 2) after subtraction of the nuclear susceptibility of the Cu nuclei. The fields, $\bigcirc$=0.3 mT and $\square$=2.7 mT, were oriented along the (0,1,1) direction. The inset shows the Brillouin fit ($g=2$, $J=7/2$ for the Gd^{3+} ion) to the 2.7 mT data. The only free parameter is the number density of magnetic moments N/V.

the calculated contribution of the nuclear magnetic susceptibility due to the Cu nuclei in the sample has been subtracted. At the lowest temperatures, long-time constants of the order of 6 h were observed. It took about 30 h for the $CeCu_6$ sample to reach its minimum temperature. The origin of this long equilibration time was partly the moderate thermal contact between sample and Ag cold finger with a conductance of only 2×10^{-9} W/K at 15 mK, but partly it must be due to an enhanced specific heat because the thermal time constants at higher temperatures were much shorter and there is no reason to believe that the thermal conductance would diminish much faster than $\propto T$. In this run the minimum temperature of the nuclear stage was 650 μK and the minimum sample temperature was certainly below 800 μK as judged from the time behavior of the signal. Scaling the conductance of the thermal connection this gives a heat leak of $\leq$15 fW to the sample.

In the second experiment the thermal coupling of sample 2 to the Ag holder was improved by a factor of 12, and demagnetization down to $B_{\text{final}}=5$ mT yielded a minimum temperature of the $PrNi_5$ stage of 420^{-10}_{+30} μK, bringing T_{sample} to 450^{-10}_{+40} μK. Susceptibility data of the second sample were also obtained in 2.7 mT down to 950($\pm$30) μK. This was the highest B/T ratio obtained in this work. The raw data for the susceptibility of the second sample is shown in Fig. 4 after subtraction of the nuclear magnetization of the copper nuclei. It clearly saturates in 2.7 mT below 1 mK.

Since we suspected that the increase of χ at low temperatures was due to magnetic impurities, the magnetization curves of $CeCu_6$ (after subtracting the plateau and multiplying with H_{ext}) were fitted with a Brillouin function of the form $M=N/Vg\mu_B JB_J(g\mu_B JB/k_BT)$. From the specifications of the Ce growth material Nd^{3+} and Pr^{3+} were the most likely candidates. But fits with the according g factors of 8/11 and 4/5 for the free ions ($^4I_{9/2}$ and $^3H_4$ ground states with $\mu_{\text{eff}}=3.62$ and 3.58 μ_B, respectively) were not possible. Anyway, these ions should have low-lying doublets from crystal-field splitting which makes the application of a free-spin model doubtful. The only rare-earth ion which has

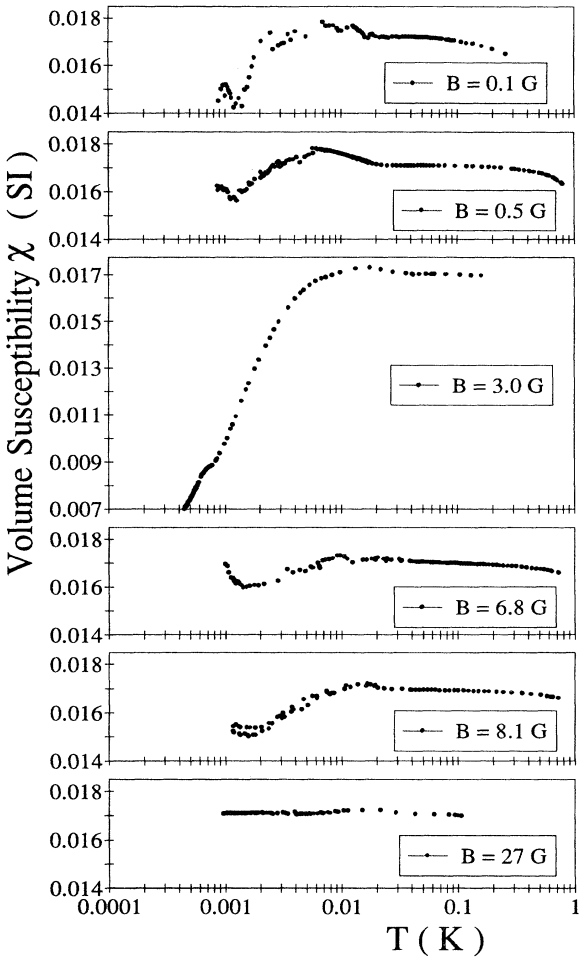

FIG. 5. Static magnetic susceptibility of single-crystalline $CeCu_6$ as obtained from the raw data after subtraction of the nuclear susceptibility of Cu and of the contribution of 1.5 ppm Gd^{3+}. The fields were oriented along the (0,1,1) direction. Data in 0.68 and 0.81 mT are from sample 1, the others from sample 2. The conversion factor of the volume susceptibility to emu/mole is 5.035.

pure spin magnetism not affected by the crystal field is Gd^{3+} (ground state $^8S_{7/2}$, $g=2$, $\mu_{\text{eff}}=7.94$ μ_B). For this state the fit was excellent for the 2.7 mT field (see inset in Fig. 4). The only free parameter in this fit is the number density N/V of the spins turning out to be 9.9(20) 10^{22} $1/m^3$ which amounts to 1.5(3) ppm of the total number of atoms present in the samples (10.5 ppm per Ce content).

In the lower fields the fit was less good showing deviations from the Brillouin function. After subtraction the Gd^{3+} contribution, however, a field-dependent structure with a decrease of χ around 3 mK is left. It is sharpest in the lowest fields, is reduced in 0.68 and 0.81 mT, and has vanished in 2.7 mT (see Fig. 5). In low fields this structure is very similar to that observed by Jin *et al.* in the ac susceptibility from different samples. At our lowest temperatures the susceptibility obtained from the magnetization in 0.3 mT decreases still further and shows a shoulder at 650 μK which could correspond to a structure at 500 μK observed by Jin *et al.*

DISCUSSION

The analysis of our susceptibility data shows that the Brillouin-like increase towards low temperatures must be due to Gd^{3+} which may have escaped detection in the Ce-starting material but which is a very likely contaminant. Its contribution masks the decrease of χ around 3 mK which shows up only after its subtraction. Since the 2.7 mT can be fitted with very high precision, the other stated rare-earth impurities present in similar contributions obviously do not play a significant role, probably due to the crystal-field splitting of their states leading to much smaller effective moments than that of Gd^{3+}. Also possible residual splittings of the Gd-ion states are not important, as this would lead to deviations from the Brillouin curve. After subtraction of the Gd contribution, the remaining susceptibility does not show a temperature dependence characteristic for other magnetic impurities and the drop in χ around 3 mK points to a cooperative antiferromagnetic ordering effect. The fact that Jin *et al.* found a similar structure in quite different samples grown from different starting material[6] makes it very likely that this structure is indicative of intrinsic magnetic ordering in $CeCu_6$ at 3 mK. Only the second structure in χ at 650/500 μK is not explained yet.

Concerning the specific-heat capacity of $CeCu_6$ we find an increase of c/T below 40 mK down to 11 mK, the lowest temperature reached for this type of experiment. Since it occurs in zero magnetic field, it cannot come from the nuclear magnetic moments and considering its size, it also cannot originate from nuclear quadrupole moments. Natural Ce has no nuclear quadrupole moment, and according to nuclear quadrupole resonance measurements,[14] the local field gradient at the Cu sites does not exceed 10^{18} V/cm^2 which means that at most 10% of the upturn at 11 mK (Fig. 2) could be due to Cu nuclear quadrupole moments. So it seems that this increase indicates the high-temperature end of the magnetic anomaly, a fact which is further supported by the enhanced time constants around 1 mK. Unfortunately, the supposed peak could not be determined more exactly in the present specific-heat experiment, and it will be hard to perform such measurements below 10 mK due to the lack of fast thermometers.

In summary, from the static magnetic susceptibility, its field dependence,and the specific-heat capacity of $CeCu_6$ at very low temperatures, we collected further evidence that $CeCu_6$ orders antiferromagnetically around 3 mK. This result is in full agreement with data on the low field ac susceptibility by Jin *et al.* As in other heavy fermion systems, also in $CeCu_6$ residual magnetic moments due to an incomplete Kondo screening of the $4f$ moments seem to exist which order through the RKKY mechanism.

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