Peculiarities of the antiferromagnetism in CeCu$_2$Si$_2$

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Abstract. We report on a detailed investigation of the magnetism in A-type CeCu$_2$Si$_2$ by neutron scattering, thermodynamic and transport measurements. The linewidths of the magnetic peaks broaden well below the Néel temperature $T_N \approx 800$ mK pointing to a finite domain size/correlation length. In contrast, within the resolution of the experiments the magnetic order is static. Complementary measurements of the electrical resistivity observed a superconducting transition at $T < 450$ mK well below $T_N$. However, no anomaly has been detected in heat capacity measurements. All results indicate that A-type single crystals exhibit parasitic superconductivity limiting the size of the antiferromagnetically ordered regions. The observed behavior can be understood by the slight off-stoichiometry of A-type CeCu$_2$Si$_2$.

1. Introduction

One of the most puzzling questions in current condensed matter physics is the relation between superconductivity and magnetism. This is especially interesting in systems where both phenomena are observed in the same temperature range. Here two cases can be distinguished: first, systems where different subsystems are responsible for magnetism and superconductivity as e.g. in $REMo_6S_8$ ($RE$: rare-earth element) or some $RENi_2B_2C$ compounds. Second, there exist also systems where the same electronic subsystem is involved into the formation of magnetic order and superconductivity. While in the former systems coexistence of both phenomena can be easily understood, the latter compounds attract special attention since competition as well as coexistence of superconductivity and magnetism is observed. Compounds belonging to this group are e.g. heavy-fermion compounds like UPt$_3$, UPd$_2$Al$_3$, URhGe, CeCu$_2$Si$_2$, and UGe$_2$, CeIn$_3$ and CeCoIn$_5$ under pressure etc. In some of these compounds superconductivity appears in the vicinity of a magnetic quantum phase transition [1, 2], i.e. when the magnetic ordering temperature is suppressed to zero. The order parameters of the magnetic order and the superconductivity have to be compatible when both phenomena coexist.

In the case of the heavy-fermion compound CeCu$_2$Si$_2$ the Ce 4f electrons do not only order magnetically but are also involved in the formation of superconducting Cooper pairs. CeCu$_2$Si$_2$
becomes superconducting below $T_c \approx 600 \text{ mK}$ as already discovered in 1979 more than 25 years ago [3]. About a decade later first hints about magnetic order in the system were found by NMR and $\mu$SR measurements [4, 5]. CeCu$_2$Si$_2$ crystallizes in the tetragonal ThCr$_2$Si$_2$ structure with lattice constants $a \approx 4.1 \text{ Å}$ and $c \approx 9.9 \text{ Å}$. The actual composition determines the ground state properties which range from antiferromagnetic order (A-type), exhibiting superconductivity (S-type) or showing both, antiferromagnetism and superconductivity (A/S-type). While the nominal stoichiometry “1:2:2” leads to A/S-type crystals, Cu excess results in S-type and Si rich samples show A-type behavior [6].

A breakthrough in the study of CeCu$_2$Si$_2$ came with the possibility to grow large single crystals with well-defined properties some years ago. Recently, the magnetic order in CeCu$_2$Si$_2$ was determined to be an incommensurate spin-density wave. For this an A-type single crystal was investigated at low temperature by neutron diffraction [7]. The experiment revealed magnetic superstructure peaks at incommensurate positions, characterized by a propagation vector $\tau$ of the magnetic order $\tau = (0.215 0.215 0.53)$ at lowest temperature $T = 50 \text{ mK}$. Magnetic intensity vanishes at $T_N \approx 800 \text{ mK}$. The propagation vector is temperature dependent above $T \approx 350 \text{ mK}$, while it stays constant below. This transition from a constant to a $T$ dependent $\tau$ is of first order as evidenced by thermal expansion measurements showing a hysteretical behavior [7]. However, the neutron measurements were limited by the signal-to-background ratio of only 1 : 1 and by the neutron flux. The background results to a considerable amount of Kondo scattering. The Kondo effect with a Kondo temperature of $T_K \approx 15 \text{ K}$ in CeCu$_2$Si$_2$ leads to a quasielastic response with a half width $\Gamma = k_B T_K \approx 1.3 \text{ meV}$. In order to suppress the intensity due to Kondo scattering neutron scattering with a good energy resolution is required. This can be achieved using a triple-axis spectrometer and neutrons with low energies (small wavevectors).

2. Experiment

Therefore subsequent neutron scattering measurements to further study the magnetically ordered state in CeCu$_2$Si$_2$ were performed on the triple-axis spectrometer IN12 at the high-flux reactor of the Institut Laue-Langevin in Grenoble. In addition, the critical scattering around the Néel temperature was investigated. All experiments were carried out with a fixed final neutron energy of $E_f = 2.74 \text{ meV}$ corresponding to a fixed final neutron wavevector $k_f = 1.15 \text{ Å}^{-1}$. Together with a double-focusing analyzer and a horizontal collimation of $52'/k_i - 60' - \text{open} - \text{open}$ ($k_i$: incident neutron wavevector) this results in an energy resolution of $\Delta E = 57 \mu\text{eV}$ (full width at half maximum) at zero energy transfer. Data were taken at temperatures between $T = 50 \text{ mK}$ and 1 K. For the measurements we used the A-type crystal with a mass $m \approx 340 \text{ mg}$ already investigated before [7]. For a detailed neutron study a second large A-type single crystal with $m \approx 1.4 \text{ g}$ was used. Both crystals are from the same batch and were grown in Cu flux. X-ray measurements on powdered pieces confirmed the tetragonal crystal structure and revealed the high quality of the single crystals. The neutron experiments were complemented by heat capacity and electrical resistivity measurements on the small A-type crystal. These measurements were performed between $T = 50 \text{ mK}$ and 1 K and in magnetic fields up to $B = 2 \text{T}$. For the heat capacity measurements a quasiadiabatic heat-pulse technique was used. The electrical resistivity was measured in a standard four-point ac geometry. Since the small A-type crystal has not the ideal shape for resistivity measurements (approx. $4.5 \times 3.5 \times 3.5 \text{ mm}^3$), the absolute accuracy of the resistivity is limited to about 20% due to the uncertainty in the geometrical factor. However, this does not affect the temperature dependence of the electrical resistivity.
3. Results and discussion

3.1. Line broadening of magnetic peaks

Fig. 1 displays some rocking scans (rotating the sample through the scattering condition while keeping the analyzer/detector fixed) across the magnetic satellite reflection at $Q \approx (0.22 \ 0.22 \ 1.47)$ in A-type CeCu$_2$Si$_2$ at different temperatures performed on the large single crystal. The expected rocking width given by the resolution of the instrument and the mosaicity of the crystal is marked as "res". Scans are shifted by 300 counts with respect to each other. Data taken at $T = 790$ mK are amplified by a factor of 2. Solid lines indicate fits with Gaussian lineshape to the data.

Fig. 2. Temperature dependence of the integrated magnetic intensity and the rocking width (FWHM, full width at half maximum) in A-type CeCu$_2$Si$_2$ (large crystal) as a result of fits to the data partly shown in Fig. 1. "resolution" displays the expected width as in Fig. 1.

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Figure 2. Temperature dependence of the integrated magnetic intensity and the rocking width (FWHM, full width at half maximum) in A-type CeCu$_2$Si$_2$ (large crystal) as a result of fits to the data partly shown in Fig. 1. "resolution" displays the expected width as in Fig. 1.
crystal [7], while iii) the temperature dependent peak width was somehow unexpected. At low temperatures, \(T = 150 \text{mK}\), the width of 1.1 deg (FWHM) is much broader than the expected rocking width given by the mosaicity of the crystal and the instrumental resolution. This width was estimated from the width of the nearest nuclear peak, the \((0 0 2)\) reflection with a temperature independent rocking width of 0.7 deg, and is denoted by "res" in Fig. 1. Surprisingly, the width reaches roughly the resolution width at \(T = 610 \text{mK}\). A detailed investigation of the linewidth of the magnetic \((0.22 0.22 1.45)\) peak was performed as a function of temperature. The reflections have been fitted by a peak with Gaussian lineshape (cf. solid lines in Fig. 1). The linewidth and the magnetic intensity as a result of these fits are displayed in Fig. 2. A small kink in the integrated intensity at \(T \approx 400 \text{mK}\) marks the onset of the temperature dependent propagation vector. Finally the intensity vanishes at \(T_N \approx 850 \text{mK}\) in good agreement to the small A-type crystal. Turning to the width a considerable broadening is observed at lowest temperatures. With increasing temperature the linewidth narrows, reaching roughly resolution width at \(T \approx 550 \text{mK}\), before again a line broadening sets in around \(T_N\) due to a finite correlation length. An estimation of the correlation length at lowest temperature \(T = 100 \text{mK}\) yields a value \(\xi \approx 130 \text{Å}\). Additional scans performed along perpendicular directions in reciprocal space across different magnetic satellite peaks confirm the line broadening. Changes in the crystal structure seem to be very unlikely as origin for the line broadening since all measured nuclear peaks do not show any change with temperature. To corroborate these findings the small A-type single crystal has been checked by rocking scans at a few selected temperatures. Scans at \(T = 400 \text{mK}\) and \(700 \text{mK}\) are shown in Fig. 3 and are in qualitative agreement with the results obtained on the large crystal. Though, the difference between both crystals is the total line broadening which is smaller in the small A-type crystal. This results in an increased correlation length of \(\xi \approx 280 \text{Å}\) at low temperatures in this crystal. Due to the coarse resolution in the first neutron diffraction experiments [7] this line broadening has not been seen before. In total, the antiferromagnetic order in both A-type single crystals is no more long-range in nature at lowest temperature, but exhibits a finite correlation length of the order of a few hundred Ångstrom. Instead of a finite correlation length one can interpret the line broadening also as a finite domain size of the antiferromagnetically ordered regions.

**Figure 3.** Rocking scans across the magnetic satellite reflection at \(Q \approx (0.22 0.22 1.45)\) in A-type CeCu\(_2\)Si\(_2\) at \(T = 400 \text{mK}\) and \(700 \text{mK}\) performed on the small crystal. "res" denotes the expected width given by the instrumental resolution and the mosaicity of the crystal as measured on nuclear peaks. The scans are shifted by 100 counts with respect to each other. Solid lines indicate fits with Gaussian lineshape to the data.
3.2. Magnetic response and critical spin dynamics

Usually a finite correlation length is accompanied by a finite lifetime of the magnetic order. Early μSR and NQR measurements on CeCu$_2$Si$_2$ powder samples found indeed indications for a dynamic nature of the magnetic order [8, 9]. Instead of being static the magnetic order was reported to fluctuate with a rate of a few MHz. To look for a finite lifetime of the magnetic order energy scans were performed at the position of the magnetic satellite peak at $Q \approx (0.22 \ 0.22 \ 1.45)$ well below the Néel temperature in the antiferromagnetic state. A finite lifetime would result in an increased linewidth $\Gamma$ in energy compared to the energy resolution of the instrument. However, no broadening of the magnetic peak could be observed in energy giving only an upper limit for the linewidth $\Gamma < 20 \mu$eV. Inelastic neutron scattering measurements with higher energy resolution are currently in preparation to look for a dynamic nature of the magnetic order.

Further inelastic neutron scattering was aimed to investigate the critical spin dynamics and a possible critical slowing down of the magnetic response around $T_N$. Therefore energy scans have been performed at several temperatures in the vicinity of $T_N$. Fig. 4 shows e.g. an energy scan taken at $Q_{AF} \approx (0.22 \ 0.22 \ 1.45)$ at a temperature $T = 950$ mK, i.e. slightly above $T_N$. The response consists of a sum of an elastic incoherent contribution and a magnetic signal. The magnetic contribution is quite weak, quasielastic and can be described by a quasielastic Lorentzian line convoluted with the instrumental resolution. The solid line in Fig. 4 displays a fit of the total response including both contributions to the data. The fits yield the staggered susceptibility $\chi(Q_{AF})$ and the linewidth $\Gamma$ in energy. The temperature dependence of both parameters can be seen in Fig. 5. The staggered susceptibility $\chi(Q_{AF})$ diverges at $T_N$ as expected. Unfortunately, the error bars are too large and the measurements not close enough to $T_N$ to determine critical exponents. On the other hand, the linewidth $\Gamma$ decreases linearly with decreasing temperature extrapolating to $\Gamma = 0$ at $T \approx 850$ mK $\approx T_N$, i.e. the magnetic
response shows a critical slowing down. Below $T = 875$ mK the magnetic signal appears to be purely elastic corresponding to $\Gamma = 0$ or an infinite lifetime within the experimental resolution.

3.3. Transport and thermodynamic measurements

To study the origin of the unusual temperature dependence of the correlation length/domain size in A-type CeCu$_2$Si$_2$, thermodynamic and transport measurements were carried out on the small A-type single crystal. Fig.6 displays the electrical resistivity as a function of temperature in several magnetic fields. In zero magnetic field no anomaly is detected at $T_N$. However, below $T = 450$ mK the resistivity decreases rapidly reaching (roughly) zero resistivity at $T \approx 150$ mK. (The very small, but finite $\rho_0 = 1 - 2 \mu$Ωcm at lowest $T$ is most likely due to contact resistance.) This transition into a superconducting state is quite broad and might indicate a percolation transition with possibly small superconducting regions yielding a superconducting path just at low temperatures. It might originate from inhomogeneities in the crystal. Upon applying magnetic field the superconducting transition is rapidly suppressed with a critical field $B_c^2 < 1.2$ T in line with results on bulk superconducting samples [10, 11].

Heat capacity measurements give further hints that the superconducting transition is not a bulk effect. The actual heat capacity measurements extend previous measurements on the same crystal [7] which were limited to $T > 0.4$ K, to much lower temperatures. Both measurements coincide in the region of overlap. The specific heat is plotted as $C/T$ versus $T$ in Fig.7 for $B = 0$ and $B = 2$ T to kill superconductivity. Nuclear hyperfine contributions to the specific heat are not subtracted from the data and are responsible for the upturn in $C(T)/T$ below $T \approx 120$ mK. The maximum in $C(T)/T$ at $T \approx 800$ mK marks the onset of the antiferromagnetic order. In contrast to the bulk superconducting samples which show a sharp maximum in $C(T)/T$ versus $T$ at the superconducting transition [3] no anomaly is visible in the data of the A-type crystal between 200 and 500 mK. In $B = 2$ T no obvious differences in $C(T)/T$ are seen below $T = 500$ mK, the region where the sample becomes superconducting. Only the transition temperature is slightly depressed. Therefore, a transition into a bulk superconducting phase in the A-type crystal can be ruled out.
3.4. Discussion
All measurements presented here, microscopic as well as macroscopic, strongly suggest that only a minority phase becomes superconducting. These superconducting regions have to be quite small since $\mu$SR has not detected any sign of superconductivity in the small A-type crystal [12]. They limit the size of the antiferromagnetically ordered regions and therefore the magnetic peaks are broadened and yield a finite correlation length. At temperatures above the superconducting transition the whole crystal is magnetically ordered. Hence, the antiferromagnetic superstructure peaks show resolution width. Since antiferromagnetism and superconductivity exclude each other on a microscopic level in this A-type single crystal of CeCu$_2$Si$_2$, the small amount of the crystal becoming superconducting would result in a small decrease of the magnetic intensity when entering the superconducting state. However, this decrease might easily be below the detection limit and might be masked by the lock-in transition which is accompanied by a spin reorientation leading also to a kink in the magnetic intensity.

The microscopic origin for a scenario with an antiferromagnetically ordered majority phase and a superconducting minority phase might be the slight off-stoichiometry of A-type CeCu$_2$Si$_2$ samples within the narrow homogeneity range where CeCu$_2$Si$_2$ forms. A-type crystals have a small Si excess and Cu deficiency [6] causing site exchange, i.e. Si atoms occupy Cu sites within the crystal structure. Hence, small inhomogeneities might lead to precipitations with slightly different composition than the main phase. They may become superconducting while the main phase remains magnetically ordered. Such a Cu/Si site exchange would not affect the long-range crystal structure, but would result locally in different electronic ground states, antiferromagnetic or superconducting.

4. Summary
We reported on a detailed investigation of the antiferromagnetic order in A-type CeCu$_2$Si$_2$ single crystals by neutron scattering, thermodynamic and transport measurements. The linewidths of the magnetic peaks broaden in reciprocal space at lowest temperature pointing to a finite domain size/correlation length. No increase of the magnetic peaks in energy has been detected, indicating static order within the resolution. In measurements of the electrical resistivity a superconducting transition has been observed at $T < 450$ mK, i.e. well below $T_N$. In contrast, no anomaly has been detected in heat capacity measurements. All results indicate that our A-type single crystals exhibit no bulk superconductivity. Only a minority phase becomes superconducting, while the majority phase remains antiferromagnetically ordered. The observed behavior can be understood by the slight off-stoichiometry and Cu/Si site exchange in A-type CeCu$_2$Si$_2$.

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5. References
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