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Magnetic structure and field-dependent properties of $CeCu_5$

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Abstract. A study of the magnetic properties of the hexagonal compound $CeCu_5$ reveals antiferromagnetic order below $T_N = 3.9$ K. The magnetic structure comprises moments along the c-axis with a propagation vector $k = [0, 0, \frac{1}{2}]$. The presence of the Kondo interaction reduces the magnitude of the moments from about $0.42\mu_B$, expected for a $|\pm\frac{1}{2}\rangle$ doublet, to about $0.36\mu_B$, observed from elastic neutron scattering experiments.

1. Introduction

The intermetallic compound $CeCu_5$ exhibits simultaneously long-range magnetic order and Kondo screening of the Ce 4f moments [1, 2]. The latter effect is evident from negative logarithmic contributions to the electrical resistivity, from a pronounced minimum in the temperature-dependent thermopower and from an enhanced value of the electronic contribution to the specific heat $c(T)$. From a c/T against T^2 plot (6 K $\leqslant T \leqslant$ 15 K) a Sommerfeld value γ of about 100 mJ mol^{-1} K^{-2} has been deduced. Specific heat measurements down to about 300 mK [3] revealed a value for γ of roughly 120 mJ mol^{-1} K^{-2}. These values are comparable to those found typically for magnetically ordered Kondo systems such as $CeAl_2$ [4, 5] or $CeCu_2$ [6, 7]. The magnetic entropy associated with the phase transition at $T = T_N$ is about $\frac{2}{3}$ of the expected value $R \ln 2$. These observations indicate that ordering in the ground state is not formed by the whole ensemble of the 4f moments; rather, a certain fraction of these moments is involved in the Kondo interaction, thus forming those heavy-quasiparticle bands which are reflected in the observed high γ value.

$CeCu_5$ is also of interest as the starting material for a series of compounds formed from the substitution of Cu by Al or Ga, which leaves the hexagonal crystal structure unchanged [8]. These substituted compounds apparently exhibit quasiparticles with enormously enhanced effective masses. For example, c/T of $CeCu_4Al$ attains a value of more than 2.8 J mol^{-1} K^{-2} at $T = 30$ mK [9]. Moreover, this substitution is responsible for the suppression of long-range magnetic order. Pronounced coherence effects, as usually found in the electrical resistivity and other transport properties, have not been detected in the substituted compounds. The destruction of coherence is referred to crystallographic disorder on the (3g) sites of the $CaCu_5$ structure although cerium forms a regular sublattice in these compounds [8].

However, the $CeCu_5$ results discussed above appear to be in contradiction to investigations performed by Alekseev *et al* [10]. Their study indicated that a peak in

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the magnetic contribution to the specific heat appears at $T \simeq 3$ K, and is quite different from the usual shape of a λ-like anomaly or mean-field-like ordering.

The aim of the present paper is to elucidate the type of magnetic order in $CeCu_5$ at low temperatures and to demonstrate the reduction of the cerium moments due to the Kondo effect. For this purpose we have performed elastic neutron scattering experiments below and above the transition temperature and additionally we have studied the field-dependent magnetization up to 12 T and at temperatures from 0.5 K to 10 K. The observed results are discussed in the scope of a modified mean field model incorporating the Kondo effect. We find that strong anisotropic exchange coupling is necessary to describe the magnetic structure of this compound.

2. Experimental details

Polycrystalline samples of $CeCu_5$ were prepared from stoichiometric quantities of the elements using high-frequency induction melting and a rather rapid cooling of the melt. A subsequent heat treatment at $T = 750\,°C$ for two weeks under an argon atmosphere ensured sample homogeneity. X-ray diffraction measurements at room temperature, using Cr Kα radiation, yield the following lattice parameters for this hexagonal compound: $a = 5.149(1)$ Å and $c = 4.108(1)$ Å. Elastic neutron scattering experiments have been performed at the Saphir reactor of the PSI, Villigen, Switzerland, using the double-axis multicounter neutron powder diffraction diffractometer DMC [11]. A ^{4}He cryostat was used to cover the temperature range down to 1.5 K. The powdered sample (about 20 g) was enclosed under an He gas atmosphere in a cylindrical vanadium tube of 10 mm diameter and 50 mm height. The high-resolution mode and neutron wavelength $\lambda = 1.6984$ Å were used. The absorption-corrected neutron profile intensities were analysed by means of a modified version of the Wiles–Young program [12], based on recently published scattering lengths [13]. For investigation of magnetic ordering, neutron diffraction measurements were performed on DMC in the high-intensity mode ($\lambda = 1.7037$ Å).

The magnetization measurements were performed at Birkbeck College, London, using an Oxford Instruments ^{3}He vibrating sample magnetometer operated at 66 Hz. Fields up to 12 T were applied over the temperature range 0.5–80 K.

3. Results and discussion

The elastic neutron diffraction pattern of $CeCu_5$ in the paramagnetic phase ($T = 12$ K) is shown in figure 1. The observed pattern agrees with the expected intensity distribution of the hexagonal $CaCu_5$ phase and confirms previously reported neutron scattering results [14]. From a refinement of these data the following lattice parameters have been obtained: $a = 5.1305(3)$ Å and $c = 4.0938(3)$ Å. The temperature factors derived from the least-squares fit are $B_{Ce} = 0.43$ Å^2, $B_{Cu}^{(2c)} = 0.15$ Å^2 and $B_{Cu}^{(3g)} = 0.04$ Å^2. Agreement values $R_{wp} = 15.21\%$ and $R_I = 11.12\%$ were derived for the weighted and integrated intensities, respectively. From the counting statistics, the expected value is calculated to be $R_e = 2.04\%$, yielding $\chi^2 = 55.72$. Small amounts of a foreign phase, evident from additional neutron diffraction pattern in the vicinity of $2\Theta \simeq 50°$, most likely leads to the unusually large value of χ^2. This can be seen from an additional fit to the neutron pattern excluding the data of the range $48° < 2\Theta < 52°$, resulting in $R_{wp} = 13.02\%$, $R_I = 9.60\%$ and $\chi^2 = 38.71$.

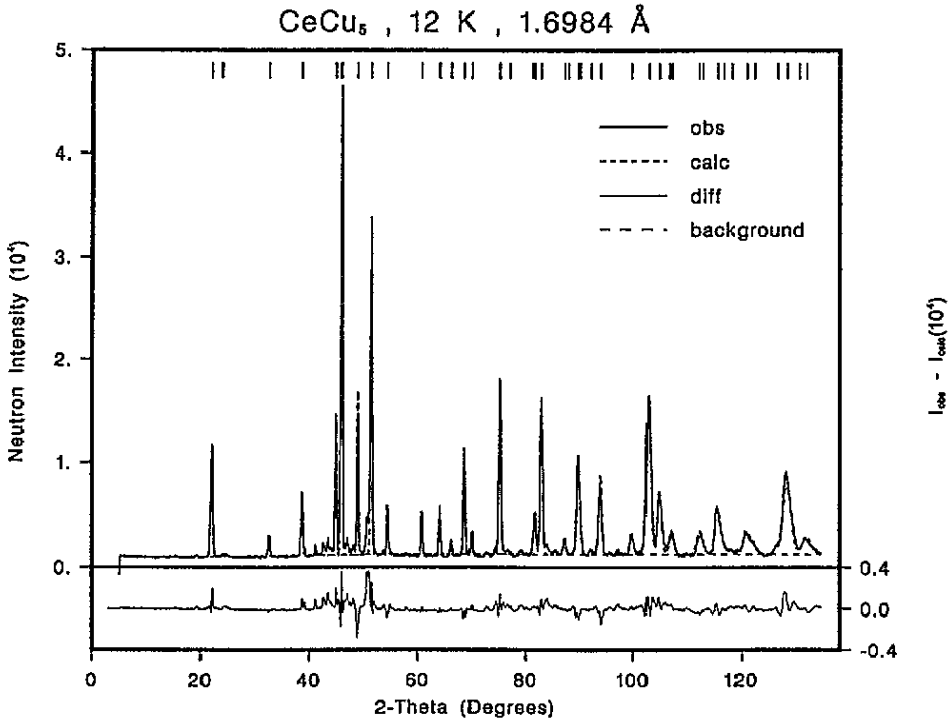

Figure 1. Observed, calculated and difference neutron diffraction pattern of paramagnetic $CeCu_5$ at $T = 12$ K (high-resolution mode).

To observe the magnetic Bragg peaks of $CeCu_5$, elastic diffraction measurements in the high-intensity mode were performed down to 1.5 K. Figure 2 shows the difference neutron diffraction pattern $I(1.5\text{ K})$–$I(5.7\text{ K})$. This difference plot clearly reveals additional magnetic intensity, indicating the presence of long-range antiferromagnetic order. The 2Θ position of the magnetic peaks shown in figure 2, with index $(0, 1, \frac{1}{2})$, $(1, 1, \frac{1}{2})$ and $(0, 1, \frac{3}{2})$, are best accounted for with a propagation vector $\boldsymbol{k} = [0, 0, \frac{1}{2}]$. A standard Rietveld analysis (without background fit) applied to the inequivalent magnetic peaks revealed an ordered moment of the Ce ion along the c-axis with $|\mu| = 0.36(4)\mu_B$ at $T = 1.5$ K. Because the magnetic structure factor associated with the $(0, 0, \frac{1}{2})$ peak is zero in the case of moments parallel to the c-direction, but has a maximum for moments perpendicular to the c-axis, we exclude from the extinction of the $(0, 0, \frac{1}{2})$ peak, expected at $2\Theta = 12.01°$, the alignment of the Ce moments perpendicular to the c-direction.

Since the magnitude of the ordered moment is much smaller than that associated with the Ce^{3+} total angular momentum $j = \frac{5}{2}$, crystal field splitting obviously governs the ground-state properties of $CeCu_5$. The crystal field of hexagonal symmetry splits the sixfold degenerate state of Ce into three doublets with eigenstates $|\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$ and $|\pm\frac{5}{2}\rangle$. Recently inelastic neutron scattering experiments on $CeCu_5$ have shown that the $|\pm\frac{3}{2}\rangle$ state is about 17 meV above the ground state, while the $|\pm\frac{5}{2}\rangle$ state most likely lies above the $|\pm\frac{3}{2}\rangle$ doublet [3, 10, 15]. From these results it is obvious that no significant contribution to the magnitude of the magnetic moment can be expected from excited crystal field levels. The magnetic moment associated with the $|\pm\frac{1}{2}\rangle$ state follows then from $\langle\mu_c\rangle = g_j\mu_B\langle\frac{1}{2}|J_z|\frac{1}{2}\rangle$; with $g = \frac{6}{7}$ the magnetic moment μ_c is expected to be $0.428\mu_B$. The calculated magnitude

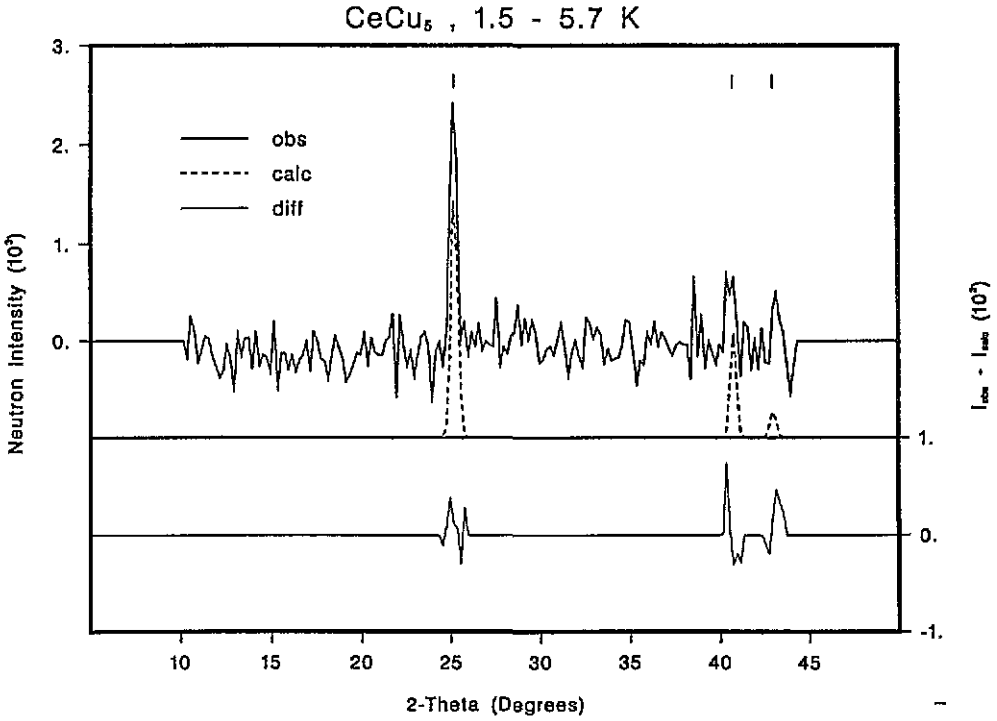

Figure 2. Magnetic difference neutron diffraction pattern $I(1.5\text{ K})$–$I(5.7\text{ K})$ of antiferromagnetic $CeCu_5$.

of the moments in the basal plane $\mu_{a,b}$ is about $1.28\mu_B$. Moments associated with the other eigenstates are $1.28\mu_B$ and $2.14\mu_B$ for $|\pm\frac{3}{2}\rangle$ and $|\pm\frac{5}{2}\rangle$ in the c direction, respectively. The fact that the magnetic moment along the c-axis attains a value of roughly $0.36\mu_B$ indicates that the ground state of this hexagonal compound is the $|\pm\frac{1}{2}\rangle$ state. The difference between the calculated and the observed value of the magnetic moment in the crystal field ground state is attributed to the Kondo effect causing a moment reduction. Within a phenomenological model, the reduction of the moments in the ordered state by the Kondo effect can be correlated to the ratio of the Kondo temperature T_K and the exchange constant J. This empirical model, which has been discussed in detail by Bredl *et al* [16], Braghta [17] and Besnus *et al* [18], is based on the resonance level model of Schotte and Schotte [19] as well as on the mean field theory. In this model, the spontaneous magnetization of an effective $j = \frac{1}{2}$ system, which is equivalent to the classical two-level system, can be written as

$$M(T) = \frac{g_j \mu_B}{2} \tanh\left(\frac{E}{2k_B T}\right). \tag{1}$$

$M(T)$ is the spontaneous magnetization, g_j the Landé factor, μ_B is the Bohr magneton and E follows in the mean field theory from

$$E = g\mu_B B_E = g\mu_B \lambda M = J\frac{M}{M_0}. \tag{2}$$

B_E refers to the strength of the molecular field, λ is the molecular field constant, J is the exchange constant and M_0 the spontaneous magnetization at $T = 0$. To derive

equation (2), only nearest-neighbour interactions are considered. Since the Kondo effect causes a broadening of the levels, equation (1) no longer holds, and we have to use [16]

$$M(T) = \frac{g\mu_B}{\pi} \operatorname{Im} \psi \left(\frac{1}{2} + \frac{\Delta + iE}{2\pi k_B T} \right) \tag{3}$$

where ψ is the Digamma function. The Kondo-derived resonance at the Fermi energy is assumed to be Lorentz like, with the width Δ being proportional to the Kondo interaction strength, i.e. $\Delta = k_B T_K$. It has been shown [17] that a state with long-range magnetic order is possible only for $|J|/T_K > \pi/2$. Below this value, the Kondo interaction dominates the ground-state properties and magnetic order is prevented.

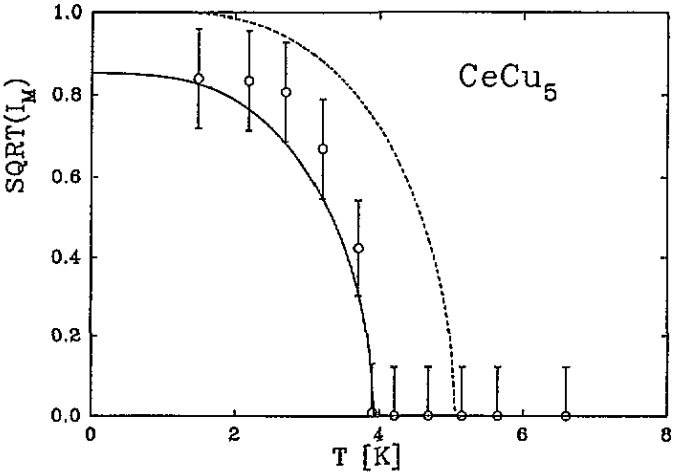

Figure 3. Normalized square root of the temperature-dependent integrated neutron intensity of the magnetic $(0, 1, \frac{1}{2})$ peak of $CeCu_5$. The solid and the dashed lines are fits according to equation (3) (see text).

The temperature-dependent magnetization $M(T)$, given by equation (3), allows us to account, at least qualitatively, for the observed behaviour of the Ce moments. In figure 3 we have plotted the temperature dependence of the square root of the observed magnetic intensity of the $(0, 1, \frac{1}{2})$ peak. Here, the neutron counts are normalized to the ratio of the calculated and observed magnitude of the moments in the crystal field ground state. Adjusting both free parameters of equation (3), i.e. the exchange constant J and the Kondo temperature T_K, allows us to describe $\mu_c(T)$ in a reasonable manner. The best agreement between the experimental data and the predictions of equation (3) is found for $J = 10.2$ K and $T_K = 2.2$ K. Both values together explain the observed 15% reduction of the magnetic moment and the ordering temperature $T_N = 3.9$ K (solid line, figure 3). Switching off the Kondo effect, i.e. setting $T_K = 0$, results in the usual Brillouin function with the full moment expected and ordering at somewhat elevated temperatures ($T_N^0 = 5.1$ K), (broken line, figure 3).

The efficiency of this phenomenological model can be demonstrated when accounting for the temperature-dependent specific heat of $CeCu_5$, reported previously [1]. In figure 4, the magnetic contribution to the specific heat c_{mag} is plotted as a function of temperature ($c_{mag} = c(CeCu_5) - c(LaCu_5)$). The anomaly in $c_{mag}(T)$ around 4 K indicates the magnetic

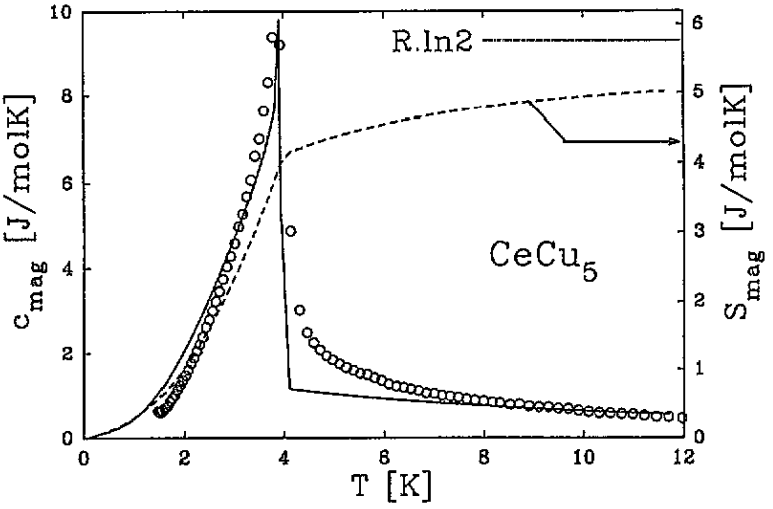

Figure 4. Magnetic contribution to the temperature-dependent specific heat c_{mag} of $CeCu_5$. The solid line is a fit according to equation (4).

phase transition. To account for this behaviour we again combine the Kondo effect and long-range magnetic order, represented in the scope of the mean field theory. The temperature-dependent specific heat, which follows from both contributions is then given by [16]

$$c_{mag}(T) = 2k_B \,\mathrm{Re}\left[\frac{z}{T}\left[1 - \left(\frac{z}{T} - \frac{\partial z}{\partial T}\right)\psi'\left(\frac{1}{2} + \frac{z}{T}\right)\right]\right] \tag{4}$$

with $z = (\Delta + iE(T))/2\pi k_B$. Using equation (4) and both parameters which have been deduced from the temperature dependence of the magnetic moments, a reasonable agreement is revealed between the fit (solid line, figure 4) and the experimental data. As expected from the experiment, the magnetic entropy at $T = T_N$ (dashed line, figure 4) is considerably smaller than $R \ln 2$. Beyond 12 K, which is more than three times the ordering temperature, this value is attained. Both short-range order effects and Kondo interaction can be made responsible for the entropy transfer to much more elevated temperatures. Furthermore, the weak temperature dependence of $S_{mag}(T)$ above T_N hints at the fact that both excited crystal field levels are well separated from the ground-state doublet; therefore, no essential Schottky contribution is found. This agrees with the available data from inelastic neutron scattering experiments on $CeCu_5$ [15].

The magnetic structure of $CeCu_5$, deduced from the present neutron study, can be described by a simple model which involves the exchange coupling between Ce ions in the same and in neighbouring planes. However, this model does not consider the Kondo effect, which reduces the values of the spontaneous moments. According to inelastic neutron scattering experiments [15] and the behaviour of the magnetic entropy of $CeCu_5$, the $|\pm\frac{3}{2}\rangle$ and the $|\pm\frac{5}{2}\rangle$ states are well separated from the $|\pm\frac{1}{2}\rangle$ ground-state doublet. Owing to these conditions, the zero-field single-ion susceptibility at low temperatures is dominated by the $|\pm\frac{1}{2}\rangle$ contribution [20]

$$\chi_a^0 = \chi_b^0 \sim \frac{9(g_J\mu_B)^2}{4kT} \tag{5}$$

$$\chi_c^0 \sim \frac{(g_J\mu_B)^2}{4kT}. \tag{6}$$

Thus, χ_a^0 is nine times larger than χ_c^0 and the system will tend to align the moments in the hexagonal plane. To prevent this possibility, which is in contradiction of our neutron diffraction results, it is necessary to introduce a strong anisotropic exchange of the form [20]

$$H_{ex} = -\tfrac{1}{2}\sum_{ij}\{J^{iso}(i-j)\boldsymbol{J}_i \cdot \boldsymbol{J}_j + J^a(i-j)(J_i^x J_j^x + J_i^y J_j^y - J_i^z J_j^z)\}. \quad (7)$$

Denoting the coupling constant within the same plane by J_s^{iso}, J_s^a and between neighbouring planes by J_d^{iso}, J_d^a (the superscripts iso and a refer to isotropic and anisotropic exchange, respectively), the magnetic ordering temperature T_N for a structure with the moments aligned in the c-direction follows from

$$4kT_N = J_s^{iso} - J_d^{iso} - (J_s^a - J_d^a). \quad (8)$$

For a structure with the moments in the hexagonal basis plane, the ordering temperature T_N' is given by

$$4kT_N' = 9(J_s^{iso} - J_d^{iso} + (J_s^a - J_d^a)). \quad (9)$$

Since the moments are aligned in the c-direction T_N must exceed T_N'. This means that $(J_s^a - J_d^a)$ has to be negative. Applying the mean field approach to a two-sublattice model, the properties of the ordered phase can be calculated. Below the ordering temperature T_N, the single-ion susceptibility and the isothermal magnetization have been calculated in the scope of a self-consistent solution of the mean field model. The coupling parameters (table 1) have been adjusted to account for the ordering temperature $T_N = 3.9$ K and, additionally, to give the correct susceptibility at $T = 6$ K.

Table 1.

J_s^{iso} (meV)	J_d^{iso} (meV)	J_s^a (meV)	J_d^a (meV)
$0.012\,03 \times 6$	-0.343×2	0	0.31×2

One parameter is not fixed by these conditions and therefore J_s^a has been chosen to be zero. To determine the exact values for the coupling parameters, it will be necessary to perform neutron scattering experiments on single crystals.

Figure 5 shows both the experimental data and the calculated temperature dependence of the magnetic susceptibility $\chi(T)$. The measured data indicate antiferromagnetic order below 3.9 K and match previously reported results [21] from which an effective magnetic moment $\mu_{eff} = 2.63\mu_B$ and a paramagnetic Curie temperature $\Theta_p = -35$ K have been deduced.

It is obvious that this model yields strong anisotropic susceptibility contributions (dashed lines, figure 5), when comparing the basal plane and the c-direction susceptibility. The solid line in figure 5 is a sum of the two contributions according to

$$\chi_{poly} = \tfrac{2}{3}\chi_a + \tfrac{1}{3}\chi_c. \quad (10)$$

Such unusually large anisotropies of magnetic properties are well known from the literature for hexagonal compounds possessing the $CaCu_5$ structure [22, 23]. In the absence

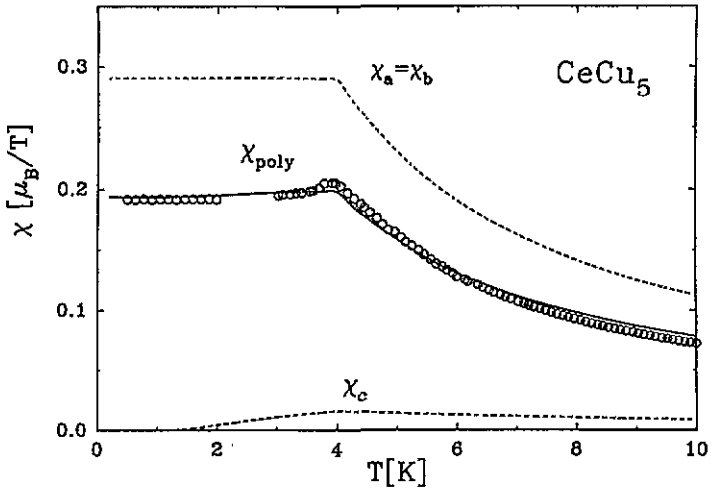

Figure 5. Magnetic susceptibility of $CeCu_5$ at low temperatures. The full line is a calculation according to a simple antiferromagnet for a polycrystalline sample. The dashed lines represent the susceptibilities along the c-axis and in the basal plane.

of results for single-crystal $CeCu_5$ samples, we assume that the susceptibility calculated for the principal directions reflects the intrinsic properties of $CeCu_5$.

Isothermal magnetization measurements have been performed up to 12 T in a temperature range from 0.5 K to 10 K. The magnetization curve taken at 0.5 K is shown in figure 6. A metamagnetic transition around 2.5 T (see inset, figure 6) characterizes $CeCu_5$ again as an antiferromagnet. At fields of 12 T, a magnetization of $0.82\mu_B$ is revealed. Calculations of the resulting moment of a polycrystalline Ce compound with hexagonal symmetry and $|\pm\frac{1}{2}\rangle$ as the crystal field ground state (compare the appendix) however yields a saturation moment of $1.05\mu_B$/Ce.

The calculated field-dependent magnetization curves based on the parameters of table 1 are shown as dashed lines in figure 6. To account for the results of a polycrystalline sample, the external field was allowed to vary in the a–c-plane while the magnetization of the polycrystal has been calculated by averaging over the different magnetizations parallel to the external field (compare the appendix). This procedure has been repeated for various values of external fields up to 20 T. As expected, the calculated magnetization in the c-direction is rather different from that of the basal plane. The direction of the easy magnetization is within the basal plane, where a value of $1.28\mu_B$ is attained in the high-field limit. This follows also from a $|\pm\frac{1}{2}\rangle$ ground state and moments aligned in the basal plane ($\langle\mu_{a,b}\rangle = \frac{1}{2}(g_j\mu_B)\langle\frac{1}{2}|J_+|-\frac{1}{2}\rangle$). On the other hand, a resulting magnetization in the c-direction requires much larger external fields and a metamagnetic transition. The high-field limit for this case is about $0.42\mu_B$, equivalent to the $|\pm\frac{1}{2}\rangle$ ground state with moments perpendicular to the basal plane.

The resulting magnetization curve ($M_{poly} = \frac{1}{3}M_c + \frac{2}{3}M_{a,b}$), shown as a full line in figure 6, exceeds the measured values. This is attributed to the Kondo effect which is not involved in the present model. However, as the field strength rises, the Kondo effect is suppressed and the moments appear to be unscreened. Extrapolating the magnetization curve at $T = 0.5$ K in a reasonable manner shows that around roughly 20 T the expected value of $1.05\mu_B$ is approached.

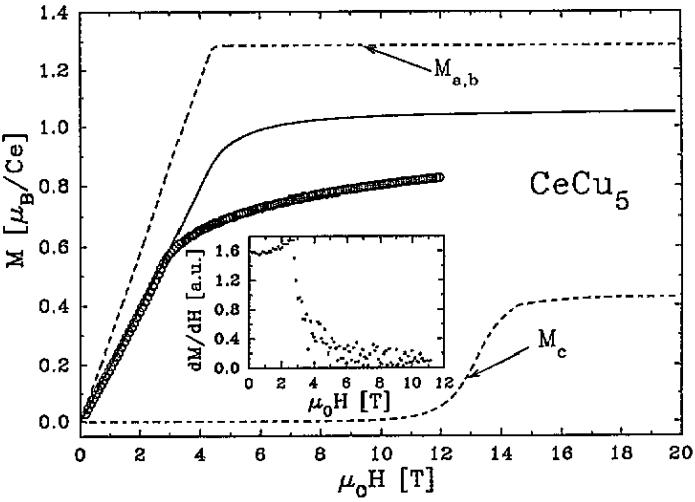

Figure 6. Magnetization of $CeCu_5$ against applied field at different temperatures. The full line represents the calculation for a polycrystalline sample as described in the text and the dashed lines are the magnetization curves for the applied field parallel to the *c*- and *a*-axes.

4. Summary

The present neutron study unambiguously indicates $CeCu_5$ as an antiferromagnetic compound with an ordering temperature $T_N = 3.9$ K. This fact, however, has already been suggested in the scope of various thermodynamic and magnetic investigations [1, 2]. Since the ordering temperature T_N deduced from those studies agrees with T_N obtained from the present neutron scattering experiments, but exceeds that reported by Alekseev *et al* [10], we believe that a simple antiferromagnetic structure, with a propagation vector $\boldsymbol{k} = [0, 0, \frac{1}{2}]$, is the ground state of this compound.

In view of Doniach's phase diagram for Kondo lattices [24], $CeCu_5$ appears to be a member of that group of compounds, where the RKKY interaction exceeds the Kondo interaction strength. Owing to this proportion, $CeCu_5$ is situated below a critical value of the s–f coupling constant multiplied by the electronic density of states. This critical parameter separates a region where long-range magnetic order and the Kondo effect coexist, from that with fully compensated moments due to enhanced Kondo interaction. A prototypic compound belonging to the latter regime is $CeCu_6$.

It is noted that the family of hexagonal uranium and cerium compounds, exhibiting a crystallographic ordered variant of the $CaCu_5$ structure, i.e. the $PrNi_2Al_3$ type, usually orders magnetically in the basal plane [25–27], while $CeCu_5$ is antiferromagnetic along the *c*-axis. The most prominent members of the former compounds are the heavy-fermion superconductors UPd_2Al_3 and UNi_2Al_3 [28, 29].

Acknowledgments

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Appendix

To calculate the saturation moment of a polycrystalline sample we first consider the effect of a magnetic field H on the ground state doublet $|\pm\frac{1}{2}\rangle$. In this case, H is a sum of the external field and the molecular field. If the direction of the magnetic field H lies in the x–z plane and the angle with the z-axis is Θ, the corresponding Zeeman Hamiltonian is

$$H_Z = -g_J\mu_B J = -g_J\mu_B H\begin{pmatrix} \frac{1}{2}\cos\Theta & \frac{3}{2}\sin\Theta \\ \frac{3}{2}\sin\Theta & -\frac{1}{2}\cos\Theta \end{pmatrix}. \tag{A1}$$

After diagonalizing this matrix, the projection of the saturation moment per ion onto the direction of the field is calculated to be

$$M_{sat}(\Theta) = g_J\mu_B\frac{\cos(\Theta)}{2}\sqrt{1+9\tan^2\Theta}. \tag{A2}$$

This saturation moment can be observed by measuring the magnetization of a single crystal when considering an applied field in the direction Θ with respect to the c-axis of the crystal. To obtain the saturation moment for polycrystalline material it is neccessary to average this moment for the different directions of the applied field. This follows from $M_{sat} = (1/4\pi)\int M(\Theta)\,d\Omega$. Then

$$M_{sat} = \int_0^{\pi/2} -d(\cos\Theta)\,M_{sat}(\Theta) = g_J\mu_B\frac{9}{8\sqrt{2}}\left(\sin^{-1}\left(\frac{\sqrt{8}}{3}\right) - \frac{\sqrt{8}}{9}\right) = 1.0536\mu_B. \tag{A3}$$

This expression is valid when k_BT is much smaller than the splitting of the doublet.

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