Probing Magnetism in CePdAl under Multi-Extreme Conditions using Polarized Neutrons

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Abstract. We have performed polarized neutron experiments on single-crystalline CePdAl at two different conditions: at 4 K and ambient pressure in a field of 9 T applied along the c-axis and at 40 mK under a pressure of 0.85 GPa and the same magnetic field. We observe that in contrast to zero field, where only two Ce atoms carry magnetic moments, in fields under different conditions all Ce moments are significantly developed. Thus, the magnetic field lifts the magnetic frustration caused by the geometry of the system. It also eliminates effects of the pressure that drives CePdAl to a quantum criticality and loss of long-range magnetic order.

1. Introduction
Geometrically frustrated systems have attracted considerable attention in recent years due to their peculiar magnetic properties [1] leading to a manifold of different ground states. The hexagonal compound CePdAl, in which the cerium moments are located on a frustrated Kagome lattice, represents a system, in which ordered and fluctuating moments coexist. It forms in the ZrNiAl type of structure (see Fig. 1) [2] and orders antiferromagnetically (AF) below $T_N = 2.7$ K [3]. The AF structure is described by an incommensurate propagation vector $q = (0.5$ 0 $\tau)$, $\tau \approx 0.35$ that is temperature dependent [4, 5] down to 1.9 K. No further magnetic phase transition is detected down to a milikelvin region [5] except for lock-in of the $\tau$ value at 1.9 K. The low-temperature specific heat coefficient is strongly enhanced ($\gamma = 250$-270 mJ mol$^{-1}$), qualifying it as a heavy-fermion system [6].

Due to the geometrical frustration of triangularly coordinated Ce atoms, only two of the three Ce atoms develop a stable magnetic moment. Both are oriented along the c axis and...
longitudinally modulated with an amplitude of about 1.7 μB. The third Ce, which is frustrated, strongly fluctuates down to at least 35mK.

Application of hydrostatic pressure shifts the anomalies connected with the appearance of the AF order to lower temperatures indicating its collapse around 1.0 GPa (see Fig. 2) [7]. On the other hand, neutron diffraction showed that the pressure destroys the magnetic order already around 0.8 GPa [8].

In this contribution we report on polarized neutron diffraction experiment on CePdAl single crystal at multiextreme conditions with the aim to check how the Ce moment recovers from different starting situations - from geometrical frustration at ambient pressure where one moment is strongly suppressed and from pressure-induced quantum critical point, where all three moments are quenched. We have determined magnetization density maps in this material at ambient pressure (at 4 K) and under pressure of 0.85 GPa (at 100 mK), both in a magnetic field of 9 T applied along the c-axis. Surprisingly spin density maps at both thermodynamic conditions do not differ drastically suggesting that the magnetic field restores in both cases a fermi-liquid behaviour in CePdAl.

2. Experimental Details

The single crystal used in the present study (in both elastic and inelastic experiments) has been prepared by a Czochralski method. It is the same one as used in our previous neutron experiments [8]. It has an irregular shape with approximate dimensions 2.5x2x4 mm³. Two kinds of diffraction experiments were performed, both at ILL Grenoble. The unpolarized neutron diffraction intensities for the crystal structure determination were collected on the hot neutrons diffractometer D9 at 4 K, i.e. above T_N. The crystal was glued on an aluminium holder and mounted in a closed-cycle refrigerator. The incident wavelength used in the unpolarized experiment was 0.824 Å.

Polarized data, here flipping ratios, were collected at low temperatures under pressure and at ambient pressure in fields up to 9 T using the diffractometer D3 on the very same crystal. The magnetic field was applied close to the c-axis, which has been found previously to be an easy magnetization direction [7]. The incident neutron wavelength was 0.825 Å and its polarization degree of 95 %. Erbium filter has been used to cut the λ/2 contamination to 10⁻⁴.

In the case of the experiment under pressure, the 1.5 GPa clamp type pressure cell made from CuBe has been used. As transmitting medium we have used fluorinert FC770. It is well known that such a transmitting medium freezes out at certain temperature upon cooling and lowers the pressure at low temperatures. While very little can be done against the first effect, it is known from experience that the pressure decreases upon lowering the temperature by about 0.25 GPa. In order to achieve the desired pressure of 0.85 GPa, the cell has been presurized at room temperature to 1.10 GPa. The cell was then placed at the tip of a dilution refrigerator capable to reach temperatures as low as 100 mK that was in turn inserted into to a superconducting vertical cryomagnet. A magnetic field of up to 9 T has been applied along the c-axis.

In order to refine the structural parameters of CePdAl, to derive the magnetic structure factors and to perform the magnetic model refinements, a suite of programs within the Cambridge Crystallography Subroutine Library [9] were used. Spin densities were determined using the software package PRIMA [10], which calculates the most probable distribution that is in agreement with the symmetry of the parent lattice, observed magnetic structure factors and associated errors using the maximum entropy (MAXENT) method [11]. The resulting magnetization densities were drawn using the computer code VESTA[12].

3. Results

A schematic representation of the non-centrosymmetric hexagonal crystal structure of CePdAl is shown in Fig. 1. This structure consists from two basal planes stacked along the c axis.
Figure 1. Schematic representation of the hexagonal crystal structure of CePdAl. The shortest in-plane Ce-Ce bonds (372 pm) are shown as well. There are two different crystallographic Pd positions denoted as Pd(1) and Pd(2), respectively. Ce atoms occupy crystallographically equivalent 3g position that splits into inequivalent positions (denoted Ce1, Ce2 and Ce3, respectively) due to magnetic ordering.

One layer contains three Ce atoms in 3g position together with one third of Pd atoms in 1b position separated by a layer built-up by Al atoms together with remaining Pd atoms (denoted as Pd(2)) in 2c position. There are two free positional parameters: the x position of Ce and Al. Each Ce has four nearest neighbours within the basal plane at a distance of 372 pm, arranged in a distorted kagome lattice. Two next-nearest Ce neighbours are found along the c-axis. Although being in an equivalent crystallographic positions, are Ce atoms in the magnetic state not equivalent. The antiferromagnetic structure consists from ferromagnetic Ce chains, separated by fluctuating Ce ions. There are three such equivalent directions resulting in an existence of three magnetic domains. All ordered Ce moments are oriented along the c-axis and their magnitudes are modulated along the c-axis.

Careful analysis of unpolarized diffraction data (1075 Bragg reflections were collected within the $0.23 \leq \sin \theta/\lambda \leq 1.10$ range) with proper corrections for absorption and extinction effects led to structural parameters that are in very good agreement with literature data [5]. The effect of the extinction was found to be very weak (few %) and the quality of the fit could not be improved by varying the occupation numbers suggesting that our crystal has a stoichiometry very close to the ideal 1:1:1 ratio. Resulting structural parameters were consequently adopted for the analysis of both, pressure and zero-pressure polarized data.

The classical polarized neutron diffraction experiment is based on collecting Bragg reflection intensities $I^+(Q)$ and $I^-(Q)$ for as many as possible scattering vectors $Q$ for an incident polarization of the beam respectively parallel (+) and antiparallel (-) to the direction of the applied magnetic field. The ratio between the two intensities (corrected for the relevant background), the so-called flipping ratio $R(Q)$, allows via the interference term between the nuclear $F_N(Q)$ and magnetic structure factors $F_M(Q)$, a precise determination of the latter values. This is even possible if $F_M(Q)$’s are much smaller than $F_N(Q)$’s, under condition that both occur at the same $Q$. For the non-centrosymmetric crystal structure, $F_N(Q)$ and $F_M(Q)$ are both complex and can be written as $F_N = F'_N + iF''_N$ and $F_M = F'_M + iF''_M$, respectively.
Figure 3. Magnetization densities in CePdAl single crystal projected approximately along the c-axis obtained using MAXENT at the two different experimental conditions. Density map reconstructed from data obtained at 4 K, ambient pressure and in a field of 9 T applied along the c-axis is shown in (a) and from data collected at 40 mK, 0.85 GPa and 9 T is shown in (b). Note that while under the former conditions all the atoms carry a moment of 1.8(1) $\mu_B$, under the later conditions, two of them carry magnetic moments of 2.0(1) $\mu_B$ and the third one (here Ce3) a reduced moment of 1.1(1) $\mu_B$.

This leads to a relatively complex expression for the flipping ratios and difficulties in deriving $F_M$’s directly from measured $R(Q)$’s. This is only possible for a sub-set of reflections having real structure factors. This follows from the fact that although the crystal structure factors can be calculated from the known $F_N(Q)$’s, one cannot determine both real and imaginary parts of $F_M(Q)$’s for a particular Bragg reflection from a single measured $R(Q)$. In addition, further assumption needs to be applied, namely that the main contributions to the spin distribution originate from electrons centered on Ce atoms. Real crystal structure factors are for space group $P\bar{6}2m$ found for reflections that obey $h = -k$, $h = 0$ or $k = 0$ relations, where $i$ is the fourth hexagonal index $i = -(h + k)$. Among those, $(4 \ 0 \ l)$ and $(11 \ 0 \ l)$ type reflections, assuming the presence of only Ce atoms, have the structure factor very small, suggesting that they are, if the majority of magnetic contribution originates from Ce atoms, are insensitive to magnetism and consequently, $R(Q)$’s are expected to be close to unity. Indeed, none of these flipping ratios deviate from 1.00 by more than $2\sigma$ for both polarized experiments. On the other hand, $(2 \ 0 \ l)$, $(5 \ 0 \ l)$ and $(7 \ 0 \ l)$ type reflections have structure factors that are large. For such reflections we observe $R(Q)$’s that deviate from unity by more than $10\sigma$, corroborates the picture that magnetic properties in CePdAl are governed by Ce atoms.

3.1. Maximum entropy method
MAXENT method is more powerful than the usual Fourier synthesis since it does not make any a priori assumption concerning the unmeasured Fourier components. As a result, it reduces both the noise and truncation effects. We have applied this method to $F_M$’s data sets calculated from $R(Q)$ with the help of known crystal structure parameters assuming a space group $P1$, i.e. treating Ce sites independently. The unit cell of CePdAl was divided into $64\times64\times32 = 131072$ cells, in which the magnetization is assumed to be constant. The reconstruction were started from a small flat magnetization distribution. As the final result, we have obtained the most probable reconstructed three-dimensional density of magnetic moment, i.e., the map which fits the data and for which the entropy is maximum. A common way to represent such a density is a projection onto a certain crystallographic plane. In Fig. 3(a) we show the projection of the magnetization densities in CePdAl single crystal approximately along the c-axis reconstructed
from data obtained at 4 K, in a field of 9 T applied along the c-axis at ambient pressure. Clearly, the magnetization is found at places of Ce atoms. Integration in three dimensions leads to a magnetic moment of 1.8(1) $\mu_B$ at all three Ce sites. In Fig. 3(b) we show projected density maps collected at 40 mK, at pressure of 0.85 GPa and 9 T. While under the former conditions all the Ce atoms carry equal magnetic moments, under pressure one of them (here Ce3) has its magnetic moment strongly reduced to a value of 1.1(1) $\mu_B$. The two remaining Ce positions show moment of 2.0(1) $\mu_B$.

3.2. Model Refinement

At first we have analyzed the experimental data by the direct refinement of the measured $R(Q)$’s of Bragg reflections with real structure factors. We assumed all the magnetic moments to be centered on the Ce ions only. These were represented by the Ce$^{3+}$ magnetic form factor $f(Q)$ that has in general orbital ($\mu_L$) and spin ($\mu_S$) parts. The magnetic amplitude of elastic neutron scattering at the scattering vector $Q$ from a magnetic ion with the moment $\mu$ is then proportional to $(\mu_L + \mu_S) f(Q) = \mu f(Q)$. The best fit to data taken without the pressure using magnetic form factor of the Ce$^{3+}$ gives an agreement factor of $\chi^2 = 4.1$. This type of fit is shown in Fig. 4. The Ce moment has been found to be $\mu = 1.63(2) \mu_B$. Moreover, a significant orbital part $\mu_L = 1.52(4) \mu_B$ has been refined leading to a strongly reduced parameter $C_2 = \mu_L / \mu = 0.93(5) \mu_B$. This value suggests a strong hybridization of the Ce 4f electrons with other states in the solid. In the next step we have treated the three Ce moments as independent quantities. The best fit leads a slightly better agreement and Ce magnetic moments that are very similar (between 1.54 and 1.71 $\mu_B$, with orbital parts between 1.51 and 1.78 $\mu_B$). This suggests that in a field of 9 T the geometrical frustration is completely lifted. Finally, we have tried also to refine a magnetic moment on the Pd sites. However, no significant magnetic contribution has been found. Refinements using the computer code Fullprof [13] yield consistent results.

The best fit to data taken under pressure yields an agreement factor of $\chi^2 = 2.6$ and an average Ce magnetic moment that is slightly larger than found without the pressure (1.67(6) $\mu_B$/Ce). The apparent difference, however, is a smaller orbital part in the case of the pressure data (1.05(8) $\mu_B$/Ce) leading to $C_2 = 0.63(9)$ suggesting that the 4f electron states are more delocalized with respect to ambient pressure state. However, a similar plot of data as a function of $\sin(\theta)/\lambda$ reveals that the data do not fall on a single curve. This can be explained by different Ce moments at different sites or by non-zero magnetic moment on the Pd/Al sites. The best fit assuming the former scenario leads to Ce moments that vary significantly between the sites (between 1.0 and 1.8 $\mu_B$ with orbital contributions being between 0.7 and 2.1 $\mu_B$). Refinements using the computer code Fullprof yield similar refined values suggesting that 4f electron states...
centered at different Ce sites experience a different delocalization degree. However, these results need to be taken with care as the pressure data were obtained with larger error bars. The inequivalency could be due to the experimental errors.

4. Discussion and Conclusions
We have performed polarized neutron experiment on single-crystalline CePdAl at two different thermodynamical conditions. Once was the CePdAl in the field-saturated state, which one achieves from a geometrically frustrated antiferromagnetical state by applying strong magnetic field. The data taken at ambient pressure at low temperatures with field of 9 T applied along the \( c \)-axis yield (achieved either by direct model refinement or via MAXENT analysis) Ce magnetic moments that are more or less equal among the originally frustrated sites. The Ce magnetic moments follow the dependence expected for the Ce\(^{3+}\) state, however, the reduced parameter \( C_2 \) indicates a strong hybridization of 4\( f \) states with other electronic states in the solid. The other thermodynamical state studied was achieved by applying pressure at very low temperature \( o \approx 100 \) mK and under pressur of 0.85 GPa. Under these conditions, in the absence of magnetic field, is CePdAl close to a quantum critical point with all the Ce moments being quenched. We observe that all the Ce moments are significantly developed when a field of 9 T is applied along the \( c \)-axis. However, first, the three sites seem to carry different moments and, second, the spin and orbital contributions seem to be very different for these sites. It is not clear, however, at the moment whether such inequivalency is a consequence of experimental uncertainties. Nevertheless, it is clear that the magnetic field lifts the magnetic frustration caused by the geometry of the system. It also eliminates effects of the pressure that drives CePdAl to a quantum criticality and loss of a long-range magnetic order.

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