Anisotropic magnetic properties and crystal electric field studies on CePd$_2$Ge$_2$ single crystal

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Abstract
The anisotropic magnetic properties of the antiferromagnetic compound CePd$_2$Ge$_2$, crystallizing in the tetragonal crystal structure have been investigated in detail on a single crystal grown by the Czochralski method. From the electrical transport, magnetization and heat capacity data, the Néel temperature is confirmed to be 5.1 K. Anisotropic behaviour of the magnetization and resistivity is observed along the two principal crystallographic directions—namely, [100] and [001]. The isothermal magnetization measured in the magnetically ordered state at 2 K exhibits a spin reorientation at 13.5 T for the field applied along the [100] direction, whereas the magnetization is linear along the [001] direction attaining a value of 0.94 $\mu_B$/Ce at 14 T. The reduced value of the magnetization is attributed to the crystalline electric field (CEF) effects. A sharp jump in the specific heat at the magnetic ordering temperature is observed. After subtracting the phononic contribution, the jump in the heat capacity amounts to 12.5 J K$^{-1}$mol$^{-1}$ which is the expected value for a spin $\frac{1}{2}$ system. From the CEF analysis of the magnetization data the excited crystal field split energy levels were estimated to be at 12.5 J K$^{-1}$mol$^{-1}$ and 230 K respectively, which quantitatively explains the observed Schottky anomaly in the heat capacity. A magnetic phase diagram has been constructed based on the field dependence of magnetic susceptibility and the heat capacity data.

(Some figures may appear in colour only in the online journal)

1. Introduction

One of the most widely investigated topics in the field of condensed matter physics is the magnetism exhibited by Ce-based intermetallic compounds. In some Ce compounds the 4f level lies in close proximity to the Fermi level, enhancing the interaction between the conduction electrons and the f electron leading to the Kondo effect which screens the 4f derived magnetic moment. The competition between the on-site Kondo effect with an energy scale $T_K \approx \exp(-1/[IN(E_F)])$ and the inter-site Ruderman–Kittel– Kasuya–Yosida (RKKY) magnetic interaction with an energy scale $T_{RKKY} \approx |J^2N(E_F)|$, where $J$ is the exchange coupling between the local moment and the conduction electrons and $N(E_F)$ is the density of states at the Fermi level, leads to various diverse ground states like magnetic ordering, valence instability, heavy-fermion nature, unconventional superconductivity etc; hence Ce-based intermetallic compounds have been widely investigated for several decades [1–17]. The CeT$_2$X$_2$ compounds, where $T$ is a transition metal and X is Si or Ge, crystallizing in the well known ThCr$_2$Si$_2$-type body centred tetragonal crystal structure, have been particularly useful in this regard. For example, heavy-fermion superconductivity is observed in CeCu$_2$Si$_2$ [1], pressure induced superconductivity in CePd$_2$Si$_2$ [2] and CeRh$_2$Si$_2$ [3, 4], CeCu$_2$Ge$_2$ [5], and unconventional metamagnetism is observed in CeRu$_2$Si$_2$ [6]. The pressure induced superconductor CePd$_2$Si$_2$ has been

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investigated in detail on a single crystal by van Dijk et al [7]. From the anisotropic magnetic studies, they observed a change in the easy axis direction from \(c\)-axis to \(a\)-axis at around 50 K. The reduced moment and a relatively large Sommerfeld coefficient \(\gamma\) in CePd$_2$Si$_2$ was attributed to Kondo effect with a strong spin fluctuation. The neutron diffraction experiments both on polycrystalline sample and single crystalline sample confirmed the antiferromagnetic ordering with the spins pointing along the [110] direction [8, 7]. On the other hand, the magnetic properties of iso-electronic CePd$_2$Ge$_2$ have been investigated only on polycrystalline samples [9–12]. Besnus et al [9] reported the magnetic and thermal properties of CePd$_2$Ge$_2$ which orders antiferromagnetically at \(T_N = 5.1\) K. They estimated the crystal field parameters from the magnetic susceptibility and from the Schottky heat capacity and inferred the crystal field split energy levels to be located at 0, 110 and 220 K corresponding to the three doublets. The magnetic structure of CePd$_2$Ge$_2$ was determined by Feyerherm et al and they found that the magnetic moment points along the [110] direction [10] similar to the case of CePd$_2$Si$_2$. Furthermore, they attributed the reduced ordered moment of CePd$_2$Ge$_2$ as not due to the Kondo effect but due to the crystalline electric field (CEF) and the anisotropic exchange interaction [10]. The effect of chemical pressure by substituting Ni in place of Pd resulted in a decrease of \(T_N\) [12] whereas the hydrostatic pressure studies on resistivity measurement revealed that the \(T_N\) increases with increasing pressure up to values as high as 10 GPa [11, 13]. In continuation of our successful efforts in growing single crystals and investigating the anisotropic magnetic properties of CeT$_2$Ge$_2$ type compounds (where T is a transition metal) like CeAg$_2$Ge$_2$ [14], CeAu$_2$Ge$_2$ [15] and CeCu$_2$Ge$_2$ [16], here we report on the anisotropic magnetic properties of CePd$_2$Ge$_2$ single crystal by measuring the transport and magnetic properties. CEF analysis has been performed on the magnetic susceptibility and heat capacity data to estimate the crystal field level splitting.

2. Experiment

The single crystal of CePd$_2$Ge$_2$ was grown by the Czochralski crystal pulling method in a tetra-arc furnace. The starting materials of Ce (99.9% purity), Pd (99.99%) and Ge (99.9999%) were taken in the stoichiometric ratio for a total mass of about 10–11 g. The sample was remelted four times to ensure proper homogeneity in a water cooled copper hearth. A polycrystalline tungsten rod was used as a seed and the crystal was pulled out of the melt at a rate of 10 mm h$^{-1}$. The pulled ingot was then subjected to powder x-ray diffraction (XRD), using a PANalytical x-ray diffractometer with monochromatic CuK\(\alpha\) radiation, to check the phase purity. Orientation of the crystal was done by the back-reflection Laue method. The dc magnetic susceptibility and the magnetization measurements were performed in the temperature range 1.8–300 K using a superconducting quantum interference device (SQUID) and vibrating sample magnetometer (VSM). The electrical resistivity was measured down to 1.9 K in a home-made set-up. The heat capacity was measured using a Quantum Design physical property measurement system (PPMS); we have also used the dilution insert of Quantum Design to measure the heat capacity down to 50 mK and in applied magnetic fields as high as 14 T.

3. Results

3.1. X-ray diffraction

To confirm the phase purity of CePd$_2$Ge$_2$ a small portion of the crystal was subjected to powder x-ray diffraction (XRD). The XRD revealed a clear pattern without any impurity peaks suggesting the phase purity of the grown crystal. A Le Bail fit was performed on the XRD pattern and the lattice constants were estimated to be \(a = 4.337\) Å and \(c = 10.051\) Å, in agreement with the previously reported values [17]. The composition of the crystal was further confirmed by energy dispersive analysis by x-ray (EDAX). In order to study the anisotropic physical properties, the grown single crystal was cut along the principal crystallographic directions, namely [100] and [001]. This was accomplished by performing a back-reflection Laue. The Laue diffraction patterns corresponding to the (100) and (001) planes are shown in figure 1. Well defined Laue diffraction spots together with the tetragonal symmetry pattern confirmed the good quality of the grown crystal. The crystal was then cut along the principal crystallographic directions using a spark erosion cutting machine for the measurement of resistivity, susceptibility and heat capacity.

3.2. Magnetization

The thermal variation of the ratio of magnetization and applied magnetic field \((M/H)\) of CePd$_2$Ge$_2$ is shown in the main panel of figure 2(a), measured in an applied magnetic field of 0.1 T in the temperature range from 1.8 to 300 K. The \(M/H\) for \(H \parallel [001]\) direction is larger than for \(H \parallel [100]\), both in the paramagnetic and in the magnetically ordered state, reflecting the anisotropy. For temperatures considerably higher than \(T_N\) the susceptibility shows Curie–Weiss like behaviour. The low temperature part of the \(M/H\) versus \(T\) plot along the three crystallographic directions [100], [110] and [001] is shown in the left inset of figure 2(a). For the field parallel to the [100] direction, the \(M/H\) exhibits a clear

![Figure 1](image-url)
cusp at 5.1 K indicating the antiferromagnetic transition at this temperature. On the other hand, the \( M/H \) versus \( T \) plot shows a kink followed by an increase at 5.1 K for the [001] direction. Similar behaviour is also observed for the isostructural CePd3S2 compound [7]. Typically in a collinear two sublattice antiferromagnet, when the field is applied parallel to the moment direction, the susceptibility will gradually decrease to zero as \( T \to 0 \), and for fields orthogonal to the moment direction the susceptibility will remain almost constant, below \( T_N \). The increase in the \( M/H \) along the [001] direction and a relatively large drop in the \( M/H \) below \( (T_N = 5.1 \text{ K}) \) in the \( ab \)-plane suggests that the [001] direction may be the hard axis of magnetization and the magnetic moment must be lying in the \( ab \)-plane as predicted by neutron diffraction experiments on polycrystalline samples [10]. From our susceptibility measurement it is obvious that the \( M/H \) falls more rapidly for \( H \parallel [100] \) direction than along the other two directions, suggesting that [100] is the easy axis of magnetization. The inverse magnetic susceptibility of CePd3Ge2 is shown in the right inset of figure 2. At high temperatures the inverse susceptibility is linear and at low temperature there is a deviation from this linearity. This deviation is attributed to the crystalline electric field effect which is discussed later. The high temperature part of the magnetic susceptibility is fitted to the Curie–Weiss law, \( \chi = \frac{C}{T-\theta_p} \), where \( C \) is the Curie constant and \( \theta_p \) is the paramagnetic Weiss temperature. We obtain \( \theta_p = -47 \text{ K} \) and \( \mu_{\text{eff}} = 2.65 \mu_B/\text{Ce} \), \( \theta_p = -46 \text{ K} \) and \( \mu_{\text{eff}} = 2.64 \mu_B/\text{Ce} \) and \( \theta_p = -5 \text{ K} \) and \( \mu_{\text{eff}} = 2.74 \mu_B/\text{Ce} \) for \( H \parallel [100], [110] \) and [001] directions, respectively. The negative sign of \( \theta_p \) suggests antiferromagnetic ordering and the effective magnetic moment is close to the free ion value of Ce3+. We also measured the susceptibility in various applied fields along the two principal crystallographic directions. It is evident from figure 2(b) that for fields parallel to the [100] direction the antiferromagnetic transition shifts to lower temperatures. For magnetic fields greater than 12.5 T, the susceptibility does not show any clear evidence of magnetic ordering down to 1.8 K. The magnetic transition becomes very broad at high fields around 14 T. On the other hand, a clear anomaly persists at low temperatures pertaining to the magnetic ordering even at fields as high as 14 T along the [110] and [001] directions. This supports the claim that the [001]-axis is the hard axis of magnetization.

The anisotropic magnetic behaviour of CePd3Ge2 was further investigated by performing isothermal magnetization measurements \( M(H) \) at a few selected temperatures. The main panel of figure 3 shows the magnetization of CePd3Ge2 at 2 K along the two principal crystallographic directions. For \( H \parallel [100], \) the magnetization initially increases linearly with the field followed by a small change in the slope at 2.4 T, and then it increases almost linearly up to 13 T at which point there is another clear change of slope indicating the spin reorientation at these two fields. On the other hand, the magnetization for the \( H \parallel [001] \) direction simply increases with the increase in field with a positive curvature and does not exhibit any evidence of spin reorientation. The magnetization along the [110] direction almost overlaps with that of the [100] direction, however the spin reorientation observed along the [100] direction is not seen. The magnetization reaches a value of 0.88 \( \mu_B/\text{Ce} \) and 0.94 \( \mu_B/\text{Ce} \) at 14 T along [100] and [001] respectively. These values of magnetization are much smaller than the theoretical value of \( gJ (\frac{5}{2} \times \frac{5}{2}) = 2.14 \mu_B \). The inset of figure 3 shows the \( M(H) \) measured at various temperatures for \( H \parallel [100] \). It is evident that the spin reorientation occurring at 13.4 T at 2 K decreases to lower values as the temperature increases. Close to the magnetic ordering temperature 5 K, the spin reorientation is not discernible.

### 3.3. Electrical resistivity

Figure 4 shows the electrical resistivity of CePd3Ge2 measured in the temperature range from 1.8 to 300 K for current parallel to the two principal crystallographic directions. There is a significant anisotropy in the electrical resistivity reflecting the tetragonal symmetry of the crystal
and most likely an anisotropic Fermi surface. The low temperature part of the electrical resistivity is shown in the inset of figure 4. The sudden drop in the electrical resistivity at 5.1 K is attributed to the antiferromagnetic ordering, which occurs due to the reduction in the spin-disorder scattering. As the sample is cooled below 300 K the resistivity decreases, as is typical of a metallic sample. The absolute value of electrical resistivity at 300 K is 77 $\mu$cm and 32 $\mu$cm for $J \parallel [100]$ and [001] respectively, which decrease to 17 $\mu$cm and 8 $\mu$cm at 1.8 K, respectively. It is to be mentioned here that in CePd$_2$Si$_2$ also the electrical resistivity is larger along the [100] direction than in the [001] direction [7]. However, unlike the case of CePd$_2$Si$_2$, where a clear $-\ln (T)$ behaviour is seen below 50 K, no such anomaly is observed in CePd$_2$Ge$_2$; this may be attributed to the larger unit cell volume compared to that of CePd$_2$Si$_2$, which does not favour the Kondo effect in the germanide. A broad hump centred around 100 K is observed along both directions which is attributed to the crystal field effect. Assuming that the excitation of spin waves in governed by the dispersion relation [18]

$$\epsilon_k = \sqrt{\Delta^2 + D k^2},$$  \hspace{1cm} (1)

where $\epsilon_k$ is the energy of the excitations, $\Delta$ is the gap in the spin-wave spectrum and $D$ is the spin-wave stiffness, the electrical resistivity in the ordered state is given by [18]

$$\rho(T) = \rho_0 + \rho_{AF}\Delta^2 \sqrt{\frac{T}{\Delta}} e^{-\frac{T}{\Delta}} \left[ 1 + 2 \left( \frac{T}{\Delta} \right) + \frac{2}{15} \left( \frac{T}{\Delta} \right)^2 \right].$$  \hspace{1cm} (2)

where the coefficient $\rho_{AF}$ is proportional to $\frac{1}{T^{1/2}}$ and $\rho_0$ is the residual resistivity which is temperature independent. Equation (2) was fitted to the low temperature electrical resistivity data of CePd$_2$Ge$_2$ below $T_N$ and the obtained fitting parameters are $\rho_0 = 16.873$ $\mu$cm, $\rho_{AF} = 0.399$ $\mu$cm K$^{-2}$ and $\Delta = 3.962$ K for $J \parallel [100]$, and $\rho_0 = 7.592$ $\mu$cm, $\rho_{AF} = 0.172$ $\mu$cm K$^{-2}$ and $\Delta = 3.814$ K for $J \parallel [001]$. Although the above equation is valid for $T \ll \Delta$, it provides a good fit to our experimental data in the magnetically ordered state right up to $T_N$. The spin-wave gap is almost the same for both the crystallographic directions and it is comparable to $T_N$ as observed in other antiferromagnet Ce compounds [19, 20].

3.4. Heat capacity

Figure 5 shows the temperature dependence of the heat capacity $C_p$ of CePd$_2$Ge$_2$ measured in the temperature range 0.05–80 K. Also shown in the main panel of figure 5 is the specific heat capacity of the non-magnetic analogue LaPd$_2$Ge$_2$ in the temperature range from 1.8 to 80 K. The observed heat capacity of LaPd$_2$Ge$_2$ is typical for a non-magnetic reference compound. The low temperature part of the heat capacity of LaPd$_2$Ge$_2$ was fitted to the expression $C/T = \gamma + \beta T^2$ to obtain the electronic specific heat coefficient $\gamma$ and the lattice contribution $\beta$. The $\gamma$ and $\beta$ were estimated to be 8.03 mJ K$^{-2}$ mol$^{-1}$ and 0.427 mJ K$^{-4}$ mol$^{-1}$. From the $\beta$ value one can estimate the Debye temperature $\Theta_D$ as 283 K, which is typical of most of the La-based compounds. The specific heat capacity of CePd$_2$Ge$_2$ shows a huge jump at 5.1 K thus confirming the bulk magnetic ordering. The $C_p$ of CePd$_2$Ge$_2$ is higher than the non-magnetic reference compound in the temperature range investigated in the present...
work. An estimate of the Sommerfeld coefficient $\gamma$ for CePd$_2$Ge$_2$ was obtained by the same method as employed for LaPd$_2$Ge$_2$ from the data below 1.7 K as shown in the lower inset of figure 5. The $\gamma$ value thus obtained is 9.17 mJ K$^{-2}$ mol$^{-1}$ which is close to that for LaPd$_2$Ge$_2$, thus indicating that the strength of the hybridization between the 4f electron and the conduction electrons in CePd$_2$Ge$_2$ is very weak. The 4f contribution to the heat capacity $C_{4f}$ was obtained by subtracting the specific heat of LaPd$_2$Ge$_2$ from that of CePd$_2$Ge$_2$. The top inset in figure 5(a) shows the $C_{4f}$, where the jump in the heat capacity at $T_N$ amounts to 12.5 J K$^{-1}$ mol$^{-1}$. In the mean field approximation the discontinuity in the magnetic part of the heat capacity for a spin $S = \frac{1}{2}$ system is given by [21]

$$\Delta C_{\text{mag}}(T_N) = 2.5 R \left[ \frac{(2S + 1)^2 - 1}{(2S + 1)^2 + 1} \right],$$

where $R$ is the gas constant. The jump in the heat capacity observed in CePd$_2$Ge$_2$ exactly matches the theoretical model. The estimated magnetic entropy obtained by integrating $C_{4f}/T$ is shown in figure 5(b). The entropy reaches 90% of $R \ln(2)$ at the ordering temperature and recovers the full value for a doublet ($R \ln(2)$) at 10 K, thus indicating a doublet ground state well separated from the first excited state. Above $T_N$ the entropy increases gradually and reaches $R \ln(4)$ for temperatures greater than 100 K. This roughly gives the estimate of the first excited state of the crystal field split level which is discussed in section 4.

Figure 6 shows the magnetic part of the heat capacity measured in various applied magnetic fields, up to 14 T with $H \parallel [100]$ direction. It is evident that the antiferromagnetic transition shifts to lower temperature, typical for an antiferromagnetic system. The shift to lower temperatures with the field corresponds well with the data depicted in figure 2(b). The peak due to antiferromagnetic order is discernible up to fields as high as 13 T, where $T_N$ has decreased down to 1.7 K. For an applied field of 14 T the peak is not seen down to 0.05 K; instead a broad hump is observed. From the log–log plot of $C_{4f}/T$, one can see from figure 6(b) that for fields greater than 12 T, the curves fall almost on a single trace in the paramagnetic region. The inset of figure 6 shows that the $C_{4f}/T$ value close to 0.05 K increases rapidly beyond 13 T. The huge increase in the low temperature $C_{4f}/T$ value may be attributed to the effect of spin reorientation that is occurring at fields greater than 13 T as observed in the magnetization for $H \parallel [100]$ in figure 3. Similar type of behaviour is also seen in CeAuSb$_2$ ($T_N = 6$ K) which exhibits a field induced quantum critical point at 5.4 T, and $C_{\text{mag}}/T$ increases rapidly in the vicinity of the critical point and shows a peak at the critical field [22].

4. Discussion

From the ($M/H$) versus $T$ plot, electrical resistivity and heat capacity measurements it is inferred that the single crystal of CePd$_2$Ge$_2$ undergoes an antiferromagnetic ordering at $T_N = 5.1$ K which is coincident with the $T_N$ of polycrystalline samples reported by Besnus et al [9, 11]. The field dependence of magnetic susceptibility and the heat capacity of single crystalline sample enabled us to construct a magnetic phase diagram which is shown in figure 7. The Néel temperature above 6 T decreases much faster along the [100] than the [110] and [001] directions. This suggests that the [001] direction is the hard axis of magnetization. Furthermore, the magnetization reaches only 0.88 $\mu_B$/Ce and 0.94 $\mu_B$/Ce for $H \parallel [100]$ and [001] directions, respectively at 14 T. These values are consistent with the neutron diffraction results on a polycrystalline sample where the ordered moment was reported to be 0.85 $\mu_B$/Ce at 1.8 K [10]. It is to be mentioned here that in the isostructural CePd$_2$Si$_2$, the ordered moment is only 0.62 $\mu_B$/Ce. This reduced value of moment in CePd$_2$Si$_2$ is attributed to the Kondo effect, where a $-\ln(T)$ behaviour is observed in the electrical resistivity and the jump in the heat capacity at the magnetic transition is lower, with the magnetic entropy amounting to 0.6–0.75 $R \ln 2$ [23, 24]. Since no such behaviour is observed in CePd$_2$Ge$_2$ the reduced value of magnetization is mainly attributed to the CEF effect.

We analysed the magnetic susceptibility and the heat capacity using the ionic CEF model. The Ce atoms in CePd$_2$Ge$_2$ occupy the 2a Wyckoff’s position and possess $D_{4h}$ tetragonal point symmetry. For tetragonal site symmetry,
for $J = 5/2$, the $2J + 1$ 6-fold degenerate level splits into three doublets. To understand the observed anisotropy in the magnetic susceptibility and to know the crystal field energy splitting, we have performed the crystal field analysis on these data. For this purpose in figure 8(a) we have plotted the susceptibility data as $1/(\chi - \chi_0)$, where $\chi_0$ was estimated as $-5.571 \times 10^{-5}$ and $1.230 \times 10^{-4}$ emu mol$^{-1}$ for $H \parallel [100]$ and [001] directions, respectively, so an effective magnetic moment of $2.54 \mu_B$/Ce is obtained for temperature above 50 K. A similar approach was taken for CePt$_3$Si and CeAg$_2$Ge$_2$ while performing the CEF analysis of the susceptibility data [25, 14]. The CEF Hamiltonian for Ce atom (with $S = 1/2$ and $L = 3$) possessing tetragonal site symmetry is given by

$$H_{CEF} = B_0^2 O_0^2 + B_4^0 O_4^0 + B_4^4 O_4^4,$$  

where $B_m^n$ and $O_m^n$ are the CEF parameters and the Stevens operators, respectively [27, 28].

The magnetic susceptibility including the molecular field contribution $\lambda_i$ is given by

$$\chi_i^{-1} = \chi_{CEF}^{-1} - \lambda_i.$$  

The expression for the magnetic susceptibility based on the CEF model is given in our previous work [26]. We have estimated the CEF parameters as given in table 1 by fitting the CEF Hamiltonian to the experimental inverse susceptibility data. Table 1 also gives the derived eigenfunctions and the

\begin{table}
\begin{tabular}{|c|c|c|c|}
\hline
Parameter & Value & Parameter & Value \\
\hline
$B_0^2$ & $5.57 \times 10^{-5}$ & $B_4^0$ & $1.23 \times 10^{-4}$ \\
$B_4^4$ & $5.00 \times 10^{-5}$ & $O_0^2$ & $2.54 \mu_B$ \\
$O_4^0$ & $1.23 \times 10^{-4}$ & $O_4^4$ & $2.54 \mu_B$ \\
\hline
\end{tabular}
\end{table}
corresponding eigen values. The solid lines in figure 8(a) are the calculated susceptibility with the unique values of the crystal field parameters. The negative value of the exchange field constant indicates antiferromagnetic interaction between Ce moments. From the obtained eigenfunctions it is observed that there is a mixing of $|\pm \frac{3}{2}\rangle$ and $|\pm \frac{1}{2}\rangle$ wave functions in the ground and second excited state while the first excited state is composed mainly of $|\pm \frac{1}{2}\rangle$. These crystal field parameters reproduce the experimental susceptibility reasonably well and are in close agreement with the parameters estimated by Besnus et al. [9] from the data obtained for a polycrystalline sample. The obtained energy levels are $\Delta_1 = 120$ K and $\Delta_2 = 230$ K. Figure 8(b) shows the isothermal magnetization plot of CePd$_2$Ge$_2$ measured at $T = 2$ K together with the calculated magnetization curves. Although the CEF calculated magnetization curves do not reproduce the experimental data, it should be noted here that the anisotropy in the magnetization along the [100] and [001] directions are clearly explained. CePd$_2$Ge$_2$ is one of the systems where the easy axis of magnetization is [100]. In the present case, although the parameter is negative, we see from our magnetization measurements that the easy axis of magnetization is in the $ab$-plane and not along the [001] direction. A similar kind of situation was observed in the isomorphic CePd$_2$Si$_2$, where the sign of the $B^0_2$ parameter was negative as determined from the magnetic susceptibility and neutron diffraction data [30, 31], while the moment lies in the $ab$-plane. A detailed neutron diffraction study on single crystal will lead to a more comprehensive understanding of the magnetic structure of CePd$_2$Ge$_2$.

The magnetic part of the heat capacity of CePd$_2$Ge$_2$, obtained after subtracting the heat capacity of LaPd$_2$Ge$_2$, shown in figure 8(c) exhibits a broad peak above 40 K which is attributed to the Schottky type excitations between the CEF levels of the Ce$^{3+}$ ions. The Schottky heat capacity for a three-level system (a ground state and two excited states) is given by the following expression:

$$C_{Sch} = \left[ \frac{R}{k_B T^2} \right] \left[ e^{(\Delta_1 + \Delta_2)/k_B T} - 2 \Delta_1 \Delta_2 + \Delta_1^2 (1 + e^{\Delta_1/k_B T}) + \Delta_2^2 (1 + e^{\Delta_2/k_B T}) \right] \times \left\{ (e^{\Delta_1/k_B T} + e^{\Delta_2/k_B T} + e^{(\Delta_1 + \Delta_2)/k_B T})^2 \right\}^{-1}, \tag{6}$$

where $R$ is the gas constant and $\Delta_1$ and $\Delta_2$ are the crystal field split excited energy levels. Having found the energy spacing for the first and the second excited doublets from the magnetic susceptibility, we have used the same energy values $\Delta_1 = 120$ K and $\Delta_2 = 230$ K in equation (6) and found that it explains the observed Schottky anomaly. The solid line in figure 8(c) shows the calculated Schottky heat capacity, thus validating our crystal field splitting estimation from the susceptibility data. The discrepancy above 50 K may be attributed to the difference in the phonon spectra of LaPd$_2$Ge$_2$ and CePd$_2$Ge$_2$ at higher temperatures.

| CEF parameters | $B^0_1$ (K) | $B^0_0$ (K) | $B^0_2$ (K) | $\lambda_1$ (emu mol)$^{-1}$ |
|----------------|-------------|-------------|-------------|-----------------------------|
| $-4.18$ | $-0.25$ | $-3.75$ | $\lambda_{[100]} = -17$ |
| $\lambda_{[001]} = -12$ |

| Energy levels and wavefunctions | $E$ (K) | $|+5/2\rangle$ | $|+3/2\rangle$ | $|+1/2\rangle$ | $|-1/2\rangle$ | $|-3/2\rangle$ | $|-5/2\rangle$ |
|---------------------------------|--------|----------------|----------------|----------------|----------------|----------------|----------------|
| $230$ | 0.8603 | 0 | 0 | 0 | 0.5098 | 0 | 0.8603 |
| $230$ | 0 | 0.5098 | 0 | 0 | 0 | 0 | 0.8603 |
| $120$ | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| $0$ | 0 | 0.8603 | 0 | 0 | 0 | 0 | 0.8603 |
| $0$ | $-0.5098$ | 0 | 0 | 0 | 0 | 0 | 0.8603 |

Table 1. CEF parameters, energy level schemes and the corresponding wavefunctions for CePd$_2$Ge$_2$. 

The application of magnetic field shifts the antiferromagnetic ordering to lower temperatures, which is more prominent along the [100] direction than along the [001] direction, as evident from the magnetic phase diagram shown in figure 7. The low value of the Sommerfeld coefficient $\gamma$ (9.2 mJ K$^{-2}$ mol$^{-1}$) in CePd$_2$Ge$_2$ which is comparable to that of LaPd$_2$Ge$_2$ indicates that the hybridization between the conduction electron and the f electron is weak and the f electrons are highly localized here. Furthermore, it is evident from the inset of figure 6(b) that the $C_{mag}/T$ increases to a large value in the magnetic field when the antiferromagnetic ordering vanishes, and this is attributed to the spin fluctuations. The enhancement in the $C_{mag}/T$ value when the antiferromagnetic ordering vanishes due to the application of magnetic field is also observed in CeAuSb$_2$, which shows a field induced quantum critical point [22]. It will be interesting to see the effect of magnetic field on the electrical resistivity of CePd$_2$Ge$_2$, down to very low temperature. This is planned for the future.
5. Conclusion

The anisotropic magnetic properties of CePd$_2$Ge$_2$ have been investigated by growing a single crystal, in a tetra-arc furnace. The phase purity and the crystal composition was confirmed by XRD and EDAX. The transport and magnetic properties have revealed large anisotropy along the two principal crystallographic directions, namely [100] and [001], reflecting the tetragonal crystal structure. The antiferromagnetic order is confirmed as $T_N = 5.1$ K. The electrical resistivity in the ordered state can be well explained by the spin-wave gap model. The Néel temperature was found to decrease with increasing field, as expected for a typical antiferromagnet system. For fields greater than 13 T, the magnetic ordering was found to vanish. Our crystal field calculation clearly explains the anisotropy in the magnetic susceptibility and the magnetization, and the energy level thus obtained for the first and second excited state was found to be 120 and 230 K. These energy levels clearly explained the Schottky anomaly in the magnetic part of the heat capacity. The jump in the magnetic part of the heat capacity was found to be 12.5 J K$^{-1}$ mol$^{-1}$ as expected from the mean field model for a spin 1/2 system. There was no signature of Kondo effect and the magnetic ordering in this system is believed to be a purely Ruderman–Kittel–Kasuya–Yosida (RKKY) type interaction. One of the interesting findings is that although the magnetization is larger along the [001] direction as observed experimentally and supported by the CEF calculation, the moment direction is orthogonal to it, oriented in the ab-plane.

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