Magnetic properties of $R_2\text{PdSi}_3$ ($R =$ heavy rare earth) compounds

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2. Comparison of the macroscopic properties of $R_2\text{PdSi}_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

In the introduction some properties of the $R_2\text{PdSi}_3$ ($R = \text{heavy rare earth}$) for which the series caused some interest have been named. The series of $R_2\text{PdSi}_3$ ($R = \text{heavy rare earth}$) has been found to be isostructural with the crystallographic structure described in the introduction (in the $P6/mmm$ space group) [Szytula1999].

Measurements of macroscopic magnetic properties on single crystals had been made for $\text{Gd}_2\text{PdSi}_3$ [Mallik1999, Saha1999, Saha2000_2], $\text{Tb}_2\text{PdSi}_3$ [Majumdar2000, Paulose2003], $\text{Dy}_2\text{PdSi}_3$ [Majumdar2001], $\text{Ho}_2\text{PdSi}_3$ [Sampathkumaran2002] and $\text{Er}_2\text{PdSi}_3$ [Iyer2005]. Summarizing, the anisotropy in the magnetic properties and the occurrence of multiple metamagnetic transitions had generated interest. Especially, the spin-glass like phase transitions found in $\text{Tb}_2\text{PdSi}_3$ and $\text{Er}_2\text{PdSi}_3$ [Paulose2003, Iyer2005] have been remarked as unusual. Citing the conclusion of Paulose et al.: “These results clearly reveal that this compound is an exotic magnetic material” [Paulose2003].

The systematic, if present, of the observed effects through the series, had not been investigated. For instance, the role of the crystal-electric field and the exchange interaction had not been separated. This chapter compares macroscopic magnetic properties of different $R_2\text{PdSi}_3$ in the paramagnetic and the ordered state. The role of the different rare earth ions is evaluated. The here presented data have partially been published [Frontzek2006].

2.1 Inverse ac-susceptibilities

Figures 2.1 to 2.6 show the real part of the zero field ac-susceptibility measurements for $R_2\text{PdSi}_3$ with $R = \text{Gd, Tb, Dy, Ho, Er and Tm}$ in the low temperature region. Both directions in-plane ($H, 0, 0$) and perpendicular to the basal plane ($0, 0, L$) (in the following addressed as crystallographic $a$- and $c$-direction) are shown. The $a$-direction is depicted with a grey color while the $c$-direction is shown in black. In figure 2.1, the left and right $y$-axis of the graph has the identical scale. In the other graphs the scale is adjusted to ideally display the zero field ac-susceptibility of both the $a$- and $c$-direction. The scale differs up to two orders of magnitude (in the case of $\text{Tb}_2\text{PdSi}_3$). $\text{Tm}_2\text{PdSi}_3$ has been measured in an inhomogeneous ac-field in a complete different ac-susceptibility setup since the normally employed ac-susceptometer allows temperatures only down to 2 K. Due to this neither a comparison of the value nor the magnitude of both curves is possible.
2. Comparison of the macroscopic properties of $R_2\text{PdSi}_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

Figure 2.1: Real part of the zero field ac-susceptibility of single crystalline Gd$_2\text{PdSi}_3$. The measurement with the ac-field along (0, 0, $L$) and ($H$, 0, 0) are shown in black and grey, respectively.

Figure 2.2: Real part of the zero field ac-susceptibility of single crystalline Tb$_2\text{PdSi}_3$. The measurement with the ac-field along (0, 0, $L$) and ($H$, 0, 0) are shown in black and grey, respectively. Mind the different values of the susceptibility (left and right $y$-axis).
2. Comparison of the macroscopic properties of $R_2\text{PdSi}_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

Figure 2.3: Real part of the zero field ac-susceptibility of single crystalline Dy$_2\text{PdSi}_3$. The measurement with the ac-field along $(0, 0, L)$ and $(H, 0, 0)$ are shown in black and grey, respectively. Mind the different values of the susceptibility (left and right $y$-axis).

Figure 2.4: Real part of the zero field ac-susceptibility of single crystalline Ho$_2\text{PdSi}_3$. The measurement with the ac-field along $(0, 0, L)$ and $(H, 0, 0)$ are shown in black and grey, respectively. Mind the different values of the susceptibility (left and right $y$-axis).
2. Comparison of the macroscopic properties of $R_2\text{PdSi}_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

Figure 2.5: Real part of the zero field ac-susceptibility of single crystalline $\text{Er}_2\text{PdSi}_3$. The measurement with the ac-field along $(0, 0, L)$ and $(H, 0, 0)$ are shown in black and grey, respectively. Mind the different values of the susceptibility (left and right $y$-axis).

Figure 2.6: Real part of the zero field ac-susceptibility of single crystalline $\text{Tm}_2\text{PdSi}_3$. The measurement with the ac-field along $(0, 0, L)$ and $(H, 0, 0)$ are shown in black and grey, respectively. The values of the susceptibility are arbitrary (also relative to each axis) due to the special measurement setup.
The comparison of the value of the ac-susceptibility for both measured directions defines the easy (hard) magnetic axis of the compound. In the following the magnetic hard (easy) direction is defined by the low (high) values of the susceptibility in the paramagnetic state.

From the positions of the absolute maxima of the respective easy magnetic axis the ordering temperatures $T_N$ have been determined and are listed in Table 1.

<table>
<thead>
<tr>
<th>R</th>
<th>$T_N$ [K]</th>
<th>$\frac{(g_J-1)^2}{J(J+1)} \cdot \mu_{\text{eff}}$ [μB]</th>
<th>$\mu_0$ [μB]</th>
<th>$\theta_L$ [K]</th>
<th>$\theta_S$ [K]</th>
<th>$\alpha \cdot 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>22.3</td>
<td>15.75</td>
<td>8.0±0.2</td>
<td>7.937</td>
<td>30.3±0.7</td>
<td>30.7±1.2</td>
</tr>
<tr>
<td>Tb</td>
<td>23.6</td>
<td>10.5</td>
<td>9.6±0.3</td>
<td>9.72</td>
<td>-32.5±1.4</td>
<td>24.0±1.4</td>
</tr>
<tr>
<td>Dy</td>
<td>8.2</td>
<td>7.083</td>
<td>10.3±0.3</td>
<td>10.65</td>
<td>-1.4±1.4</td>
<td>11.5±1.4</td>
</tr>
<tr>
<td>Ho</td>
<td>7.7</td>
<td>4.5</td>
<td>10.2±0.3*</td>
<td>10.61</td>
<td>-</td>
<td>4.3±1.4*</td>
</tr>
<tr>
<td>Er</td>
<td>7.0</td>
<td>2.55</td>
<td>9.4±0.2</td>
<td>9.58</td>
<td>15.2±1.1</td>
<td>-7.5±1.1</td>
</tr>
<tr>
<td>Tm</td>
<td>1.8</td>
<td>1.2</td>
<td>7.5±0.2</td>
<td>7.56</td>
<td>19.1±0.6</td>
<td>-15.6±0.6</td>
</tr>
</tbody>
</table>

Table 1: Compilation of results of the Curie-Weiss analysis for $R_2\text{PdSi}_3$ and theoretical values for $R^{3+}$ ions:
- $T_N$ Néel temperature determined from experiments;
- $\frac{(g_J-1)^2}{J(J+1)} \cdot \mu_{\text{eff}}$ DeGennes factor;
- $\mu_0$ effective paramagnetic moment from the Curie-Weiss analysis.
- $\theta_L$ and $\theta_S$ asymptotic paramagnetic Curie temperatures from the Curie-Weiss analysis for the measurements parallel $c$ and $a$, respectively;
- $\alpha$ Stevens parameter from reference [Hutchings1964]
* For Ho$_2$PdSi$_3$ only the values for the $a$-axis are considered (see text);

Below $T_N$ the $c$-axis is the easy magnetic axis for the compounds with $R =$ Dy, Ho and Er while it is the magnetic hard axis for $R =$ Gd and Tb. The magnetic easy axis of Tm$_2$PdSi$_3$ cannot be determined from the special ac-susceptibility setup. The compounds with $R =$ Dy, Ho and Er order at $T_N =$ 8.2 K, 7.7 K and 7.0 K, respectively, while the Tb compound has the highest ordering temperature of the whole series with $T_N =$ 23.6 K. These temperatures are in agreement with the previously reported values from powder measurements [Szytula1999, Kotsanidis1990]. Interestingly, the ordering temperatures of the series do not obey a DeGennes scaling law [DeGennes1962]. Figure 2.7 shows the comparison of the ordering temperatures and the DeGennes factor for the different $R_2\text{PdSi}_3$ compounds. Four compounds show an additional anomaly below $T_N$ in the investigated temperature range which probably corresponds to a second phase transition. These four compounds are Tb$_2$PdSi$_3$, Ho$_2$PdSi$_3$, Dy$_2$PdSi$_3$ and Er$_2$PdSi$_3$. In Tb$_2$PdSi$_3$ the broad maximum at about 10 K has been connected to a spin-glass like transition [Paulose2003]. The additional anomaly in Ho$_2$PdSi$_3$, a maximum observed for both easy and hard axis, is found around 2 K. In Dy$_2$PdSi$_3$ a kink is observed in
the easy direction while in the hard direction a strong reduction of the signal is found around 2 K. For Er2PdSi3 the anomaly has been attributed to a spin-glass like transition at $T = 2$ K [Iyer2005].

Figures 2.8 to 2.13 show the inverse ac susceptibility vs. temperature for $R_2PdSi_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$). At high temperatures the susceptibility is described by a Curie-Weiss law:

$$\chi = \frac{C}{T - \theta_p}$$  \hspace{1cm} (12)

The light grey lines represent a Curie-Weiss fit used to yield the asymptotic paramagnetic Curie temperatures $\theta_p$ for each crystallographic direction (in the following labeled $\theta_a$ and $\theta_c$ for the asymptotic-paramagnetic Curie temperature in the crystallographic $a$- and $c$-direction, respectively). The antiferromagnetic transition temperatures determined from the maximum of the ac-susceptibility curves (see figure 2.1 to 2.6) are marked by an arrow in Figs. 2.8 to 2.13.

The inverse zero-field ac-susceptibilities up to 300 K for the crystallographic $a$- and $c$-direction on Gd$_2$PdSi$_3$ are shown in figure 2.8. The paramagnetic properties of Gd$_2$PdSi$_3$ above the ordering temperature of 22 K are isotropic within the experimental variance. This is expected since Gd$^{3+}$ is an $S$-state ion and is not susceptible to the crystal electric field effect.
2. Comparison of the macroscopic properties of $R_2$PdSi$_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

Roughly above 55 K the course of the inverse susceptibility can be effectively described by a Curie-Weiss behavior. The effective paramagnetic moment is $\mu_{\text{eff}} = 8.0 \mu_B$ in excellent agreement with the expected value of $\mu_{\text{th}} = 7.937 \mu_B$ [Hund1925]. The asymptotic paramagnetic Curie temperature is around +30 K. The surprisingly large positive value of $\theta_p$ indicates ferromagnetic correlations of the antiferromagnetically ordering compound. The values of the effective paramagnetic moment and the asymptotic paramagnetic Curie temperatures are summarized in table 1.

In the case of Er$_2$PdSi$_3$ (Fig. 2.9) the magnetic hard axis is the $a$-axis and the magnetic easy axis is the hexagonal $c$ axis. This behavior is associated with a prolate shape of the 4f-charge distribution of the trivalent Er$^{3+}$ ion with a positive Stevens factor $\alpha > 0$ (see table 1). Above 50 K (corresponding to seven times $T_N$) paramagnetic behavior according to the Curie-Weiss law is found for both axes (fit from 50 K to 250 K). The anisotropy between magnetic hard and easy axis is well pronounced, yielding a small negative $\theta_a$ and a larger positive $\theta_c$ (see table 1). The slopes of both inverse susceptibility curves are equal resulting in an experimental paramagnetic moment of $\mu_{\text{eff}} = 9.4 \mu_B$ in good agreement with the theoretical free-ion value for Er$^{3+}$ ($\mu_{\text{th}} = 9.58 \mu_B$).

In contrast to Er$_2$PdSi$_3$ one observes for the Tb$_2$PdSi$_3$ compound (Fig. 2.10) that the magnetic easy axis is the in-plane $a$-axis and the magnetic hard axis is the hexagonal $c$-axis. The interchange of magnetic easy and hard axis corresponds to the opposite sign of the Stevens factor $\alpha$ of Tb$^{3+}$ ($\alpha < 0$) in comparison to Er$^{3+}$. The anisotropy found for the Tb$_2$PdSi$_3$
2. Comparison of the macroscopic properties of $R_2\text{PdSi}_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

The macroscopic properties of $R_2\text{PdSi}_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$) compound is even more pronounced than for the $\text{Er}_2\text{PdSi}_3$ compound. One observes for the magnetic easy axis paramagnetic Curie-Weiss behavior right above the ordering temperature of 23.6 K while a deviation from the Curie-Weiss law is observed in the magnetic hard direction up to 100 K (4 times $T_N$). For temperatures above 100 K the slopes of the inverse susceptibility curves for both directions are equal. The paramagnetic moment from the Curie-

Figure 2.9: Inverse $\text{Er}_2\text{PdSi}_3$ single crystal ac-susceptibility data along the $(0, 0, L)$ and $(H, 0, 0)$ direction. The Néel temperature is marked.

Figure 2.10: Inverse $\text{Tb}_2\text{PdSi}_3$ single crystal ac-susceptibility data along the $(0, 0, L)$ and $(H, 0, 0)$ direction. The Néel temperature is marked.
2. Comparison of the macroscopic properties of $R_2\text{PdSi}_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

Weiss fit is $\mu_{\text{eff}} = 9.68 \mu_B$ in good agreement with the free-ion value of Tb$^{3+}$ ($\mu_{\text{th}} = 9.72 \mu_B$). The asymptotic paramagnetic Curie temperature is positive for the $a$-direction and negative for the $c$-direction.

The anisotropic $4f$-charge distribution of the rare earth ions Dy$^{3+}$ and Ho$^{3+}$ (both having $\alpha < 0$) is expected to produce the same anisotropy as for the Tb$_2\text{PdSi}_3$ compound although less pronounced because of the smaller values for $\alpha$. In the case of Dy$_2\text{PdSi}_3$ (figure 2.11) the expected anisotropy as well as the Curie-Weiss behavior is found for temperatures above 70 K (9 times $T_N$). The observed anisotropy for Dy$_2\text{PdSi}_3$ is smaller than for Er$_2\text{PdSi}_3$ though the magnitude of $\alpha$ is larger. The analysis of the linear behavior yields an effective magnetic moment of $\mu_{\text{eff}} = 10.3 \mu_B$ which is insignificantly smaller than the free-ion value for Dy$^{3+}$ ($\mu_{\text{th}} = 10.64 \mu_B$). The behavior is characterized by a positive asymptotic paramagnetic Curie temperature for the $a$-direction while the Curie temperature for the $c$-direction is negative but close to zero. Below 70 K a deviation from the Curie-Weiss behavior is observed leading to a crossing point at around 25 K, well above the ordering temperature of $T_N = 8.2$ K. Below 25 K the $a$-axis is the magnetic hard axis while the $c$ axis has become the magnetic easy axis.

From the magnitude of $\alpha$, Ho$_2\text{PdSi}_3$ (fig. 2.12) is expected to show a small anisotropy. In figure 2.12 the inverse susceptibility curves have different slopes for the two crystallographic directions. This unusual behavior yields $\mu_{\text{eff}} = 10.2 \mu_B$ and $9.6 \mu_B$ for the $a$- and $c$-direction, respectively. The value for the $c$-direction is significantly lower than the free ion value for

![Figure 2.11: Inverse Dy$_2\text{PdSi}_3$ single crystal ac-susceptibility data along the (0, 0, $L$) and $(H, 0, 0)$ direction. The Néel temperature is marked.](image-url)
2. Comparison of the macroscopic properties of $R_2$PdSi$_3$ ($R = \text{Gd, Tb, Dy, Ho, Er, Tm}$)

$\text{Ho}^{3+}$ ($\mu_{\text{th}} = 10.61 \ \mu_\text{B}$) while the value for the $a$-direction is only slightly below that value. Therefore, for $\mu_{\text{eff}}$ of Ho$_2$PdSi$_3$ we have only used the latter value (see table 1). In addition, no value for $\theta_k$ is listed in Table 1. In the high temperature regime the $a$-axis is the magnetic easy axis as one would expect from the negative sign of the Stevens factor. At a temperature of about 40 K one observes a crossing of the inverse susceptibilities. Below 40 K the $a$-axis becomes the magnetic hard axis while the $c$ axis becomes the magnetic easy axis.

Tm$_2$PdSi$_3$ (fig. 2.13 on the next page) undergoes a magnetic transition around 1.8 K. This transition was confirmed by an additional specific heat measurement (see inset of fig. 2.13). The magnitude of the Stevens factor $\alpha$ for the Tm$^{3+}$ ion is the same as for the Tb$^{3+}$ ion but with opposite sign. Therefore, the anisotropy is similarly pronounced as in the case of the Tb$_2$PdSi$_3$ compound. Because of the opposite sign of the Stevens factor the $a$-axis is the magnetic hard axis and the $c$ axis is the magnetic easy direction as in the Er$_2$PdSi$_3$ compound. Above a temperature of 80 K for the easy $c$ axis and above 25 K for the hard $a$-axis the susceptibility is in accordance to a Curie-Weiss law. Interestingly, in the other investigated compounds the temperatures for which deviation from a Curie-Weiss behavior is observed are lower for the easy and higher for the hard direction in contrast to Tm$_2$PdSi$_3$. The Curie-Weiss fit yields an effective moment of $\mu_{\text{eff}} = 7.5 \ \mu_\text{B}$ which agrees well with the expected value for Tm$^{3+}$ ($\mu_{\text{th}} = 7.58 \ \mu_\text{B}$).