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Magnetic properties and magnetic structures of R$_2$PdGe$_6$ (R = Pr, Nd, Gd-Er) and R$_2$PtGe$_6$ (R = Tb, Ho, Er)

Bogusław Penc$^a$, Stanisław Baran$^{a,b}$*, Andreas Hoser$^b$, Janusz Przewoźnik$^c$, Andrzej Szytula$^a$

$^a$ M. Smoluchowski Institute of Physics, Jagiellonian University, Lojasiewicza 11, 30-348, Kraków, Poland
$^b$ Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner Platz 1, D-14109 Berlin, Germany
$^c$ AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Department of Solid State Physics, Al. Mickiewicza 30, 30-059 Kraków, Poland

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ABSTRACT

Polycrystalline samples of the intermetallic compounds R$_2$PdGe$_6$ (R = Pr, Nd, Gd-Er) and R$_2$PtGe$_6$ (R = Tb, Ho, Er) have been studied using X-ray diffraction as well as magnetometric and neutron diffraction measurements. All compounds have an orthorhombic crystal structure of the Yb$_2$PdGe$_6$-type (space group Cmca) and are antiferromagnetic with the Neél temperatures ranging from 4.9 K for Er$_2$PtGe$_6$ up to 48 K for Tb$_2$PdGe$_6$. The magnetic properties and specific heat data collected for Nd$_2$PdGe$_6$ show the presence of an additional phase transition below $T_N$ at $T = 4$ K. Based on the neutron diffraction data, the magnetic structures have been determined for R$_2$PdGe$_6$ (R = Pr, Nd, Tb, Dy, Ho) and R$_2$PtGe$_6$ (R = Tb and Er). Both the magnetic properties and neutron diffraction data indicate that the magnetic moment is localized on rare earth atoms. The magnetic unit cell is equal to the crystal one, however, individual compounds show different types of magnetic orderings. Magnetic moments in Pr$_2$PdGe$_6$ form a non-collinear antiferromagnetic structure at low temperatures with magnetic moments confined to the (001) plane. The low temperature magnetic structure in Nd$_2$PdGe$_6$ is a collinear antiferromagnetic one with moments parallel to the b-axis and coupled ferromagnetically within the (001) plane, while along the c-axis the moments follow the +−+− sequence. With increasing temperature, a transition to a modulated magnetic structure is observed in Nd$_2$PdGe$_6$ at $T = 4$ K. The magnetic moments in R$_2$PdGe$_6$ (R = Tb, Dy, Ho) and Tb$_2$PtGe$_6$ assume a non-collinear antiferromagnetic order within the (001) plane with the +−++−−− sequence of signs of the moments in the neighboring planes along the c-axis. The Er moments in Er$_2$PtGe$_6$ form a collinear magnetic structure with magnetic moments oriented along the a-axis and coupled ferromagnetically within the (001) plane. Along the c-axis the moments follow the +−+−+−− sequence. The magnetic structures determined here are discussed on the basis of the competition between the RKKY-type interactions and influence of Crystalline Electric Field.

1. Introduction

Ternary intermetallics composed of rare-earth elements, transition d-metals and p-electron elements attract special attention mainly due to a wide variety of chemical composition, crystal structure and interesting magnetic properties. One of the most interesting groups are ternary compounds of a general formula R$_2$TGe$_6$, where R is a rare earth element and T is a d-transition element. These compounds, originally synthesized with T = Cu, crystallize in an orthorhombic crystal structure of the Ce$_2$CuGe$_6$-type (space group Amm2, No. 38) [1]. The same type of a crystal structure was later found for the compounds with T = Pd, Pt, Ag, Au [2]. More recent single crystal data for R$_2$TGe$_6$ (R = Y, Ce, Pr, Nd, Dy, Er, Yb and Lu; T = Pd, Pt) suggest a new type of an orthorhombic crystal structure with lattice parameters: 2a, 2b and c with respect to the previous model, and the Cmca space group (No. 64) [3–7].

Magnetic data have been collected for the R$_2$NiGe$_6$ and R$_2$CuGe$_6$ compounds with R = Ce, Pr, Nd, Gd-Tm. These compounds are antiferromagnets at low temperatures [2,8–11]. For some of them also their magnetic structures have been determined [12–15]. The magnetic moments are found to be localized exclusively on the rare-earth elements. For Nd$_2$TGe$_6$ (T = Ni and Cu) and R$_2$NiGe$_6$ (R = Tb, Ho and Er) they form a simple collinear magnetic structure with the magnetic unit cell identical to the crystal one while R$_2$CuGe$_6$ (R = Ho and Er) have a magnetic unit cell doubled along the a-axis. Temperature dependence of the electrical resistivity indicates a metallic behavior of R$_2$TGe$_6$
3. Results

Magnetic properties have been reported for only a few Pd- and Pt-based compounds. The R2PdGe6 compounds are antiferromagnets with the Néel temperatures equal to 11.5 K (Ce) [2,18,19], 14 K (Pr) [20,21], 30 K (Sm) [22], 34 K (Gd) and 48 K (Tb) [21] and 25 K (Dy) [6]. La2PdGe6 is a Pauli paramagnet [6], while Yb2PdGe6 is an intermediate valence material with a highly unstable 4f shell of the Yb ions [5,22]. Also some of the R2PtGe6 compounds are antiferromagnets with the Néel temperature equal to 9.9 K (Ce) [18] and 23 K (Sm) [22]. Yb2TGe6 (T = Pd and Pt) have been found to be Pauli paramagnets [23].

In order to investigate the influence of the T element on the magnetic properties, including the magnetic order, we have performed a systematic investigation of the polycrystalline samples of selected compounds with T = Pd and Pt by measuring DC magnetic susceptibility and magnetization as well as performing neutron diffraction experiments. Out of these data, information has been extracted on the crystal structure and on the dependence of magnetic properties, including magnetic structures, on temperature.

2. Experiment

Large samples of R2PdGe6 (R = Pr, Nd, Gd-Er) and R2PtGe6 (R = Tb, Ho, Er) (~5 g each) were prepared by arc melting of pure elements taken in stoichiometric ratio (element purity: 3 N for all R, 4 N for Pd and Pt and 5 N for Ge). The samples were annealed at 870 K in evacuated quartz tubes for one week and then quenched in cold water.

For the Nd2PdGe6 compound an additional heat capacity study was carried out by a two-tau relaxation method in the temperature range 2–114 K.

Neutron diffraction patterns were collected at different temperatures using the wavelength of $\lambda = 2.4315 \text{ Å}$ on the E6 diffractometer (BER II reactor, BENSCL, Helmholtz-Zentrum-Berlin). The Rietveld-type program FullProf [24] was used for processing the diffraction data.

The quality of the samples was checked by X-ray powder diffraction at room temperature with Cu Kα radiation on X'Pert PRO X-ray diffractometer. Magnetic measurements were performed in the temperature range 1.9–390 K on a vibrating sample magnetometer (VSM) option of the Physical Property Measurement System (PPMS) by Quantum Design. DC magnetic susceptibility measurements were carried out in applied magnetic fields of 50 Oe and 1 kOe while isothermal hysteresis loops were collected at $T = 1.9$ K in the external magnetic fields up to 90 kOe.

For the Tb2PdGe6 compound an additional heat capacity study was carried out by a two-tau relaxation method in the temperature range 2–114 K.

Neutron diffraction patterns were collected at different temperatures using the wavelength of $\lambda = 1.5418 \text{ Å}$ on a vibrating sample magnetometer (VSM) option of the Physical Property Measurement System (PPMS) by Quantum Design. DC magnetic susceptibility measurements were carried out in applied magnetic fields of 50 Oe and 1 kOe while isothermal hysteresis loops were collected at $T = 1.9$ K in the external magnetic fields up to 90 kOe.

The temperature dependence of the reciprocal magnetic susceptibility is displayed in Fig. 2a–j. In a broad temperature range a linear dependence is observed, described by the Curie-Weiss formula: $\chi(T) = C/(T - \Theta_0)$. In this equation $C$ refers to a Curie constant, which is related to the effective magnetic moment by formula $\mu_{\text{eff}} = (8C)^{1/2}$,
Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility of a) Pr$_2$PdGe$_6$, b) Nd$_2$PdGe$_6$, c) Gd$_2$PdGe$_6$, d) Tb$_2$PdGe$_6$, e) Dy$_2$PdGe$_6$, f) Ho$_2$PdGe$_6$, g) Er$_2$PdGe$_6$, h) Tb$_2$PtGe$_6$, i) Ho$_2$PtGe$_6$ and j) Er$_2$PtGe$_6$ measured at the external magnetic field of 1 kOe. The insets: the upper ones – temperature dependence of the magnetic susceptibility at low temperatures taken at 50 Oe (ZFC and FC) and at 1 kOe (ZFC); the lower ones – hysteresis loop between $-90$ kOe and 90 kOe at $T = 1.9$ K.
Table 2

Magnetic data for the R2PdGe6 (T = Pd, Pt) compounds. T\text{N} refers to the Néel temperature; \(\theta_p\) is the paramagnetic Curie temperature; \(\mu_{eff}\) is the effective magnetic moment; \(\mu_e\) is the moment at \(T = 1.9\) K and H = 90 kOe determined by magnetization measurements (M) and by neutron diffraction at the lowest temperature (ND); next to the experimental (exp), the theoretical (theor) values are shown for reference. Hcr is the critical magnetic field from magnetometric measurements and DMM is the direction of the magnetic moment as determined from neutron diffraction. R\text{magn} is the magnetic reliability factor.

| R    | T\text{N} [K] | \(\theta_p\) [K] | \(\mu_{eff}\) \([\mu_B]\) | \(\mu_e\) \([\mu_B]\) | \(\mu_e\) [kOe] | Hcr [kOe] | DMM | R\text{magn} [%] | Ref.     |
|------|--------------|-----------------|----------------|-------------|----------------|----------|-----|----------------|----------|
| Ce   | 11.5         | -16             | 2.52           | 2.54        | 0.90           | 2.14     | 11  |                   | [2,18,19]|
| Pr   | 13           | +1.1            | 3.56           | 3.58        | 1.35           | 2.82(5)  | 3.20| 14               | in plane \(\alpha-b\) | 9.4     | this work     |
| Nd   | 6.5          | -3.5            | 3.60           | 3.62        | 1.91           | 2.11(2)  | 3.27| 16, 31           | \(\|b\) | 7.3     | this work     |
| Sm   | 30           | -11.6           | 8.01           | 7.92        | 1.95           | 7.00     | 35  |                   | \(\|b\) | 5.4     | this work     |
| Gd   | 38           | -29             | 9.85           | 9.72        | 1.60           | 8.64(7)  | 9.00| > 90             | in plane \(\alpha-b\) | 8.6     | this work     |
| Tb   | 28           | -10.1           | 10.56          | 10.65       | 4.87           | 7.80(8)  | 10.00| 43               | in plane \(\alpha-b\) | 6.4     | this work     |
| Dy   | 11.8         | -1.4            | 10.36          | 10.61       | 6.86           | 8.39(7)  | 10.00| 19               | in plane \(\alpha-b\) | 6.4     | this work     |
| Ho   | 6.2          | -3.1            | 9.37           | 9.58        | 5.94           | 7.58(9)  | 9.00| 11               |                   | 6.9     | this work     |
| Er   | 9.9          | -7.0            | 2.43           | 2.54        | 1.82           | 2.14     | 1.1 |                   |                     | 18      |           |
| Sm   | 23           | -10.8           | 9.83           | 9.72        | 2.18           | 8.86(6)  | 9.00| 82               | in plane \(\alpha-b\) | 2.7     | [22]        |
| Tb   | 44           | -18             | 10.47          | 10.61       | 6.52           | 10.00    | 16  |                   |                     | 18      |           |
| Ho   | 9.5          | -4.2            | 10.47          | 10.61       | 6.52           | 7.58(9)  | 9.00| 10               | \(\|a\) | 6.9     | this work     |
| Er   | 4.9          | -2.8            | 9.56           | 9.58        | 6.10           | 7.58(9)  | 9.00| 10               | \(\|a\) | 6.9     | this work     |

Fig 3. Temperature dependence of the specific heat of Nd2PdGe6 in the temperature range of 2–114 K. The solid line represents the phononic contribution, as discussed in the text. The inset presents the low-temperature part of the \(C_m/T\) (dots) and magnetic entropy \(S_m\) (solid line).

Table 3

The Debye \((\theta_D)\) and Einstein \((\theta_E)\) temperatures together with the anharmonic coefficient \((\alpha)\). These were obtained from the fitting of the formula describing phononic contribution to the \(C_p\) vs. \(T\) dependence for Nd2PdGe6 (see Fig. 3). \(m_i\) denotes multiplicities of the \(\theta_D\) parameters.

| Parameter          | Value  | \(m_i\) |
|--------------------|--------|---------|
| Debye temperature \(\theta_D\) [K] | 145(5) |         |
| Einstein temperatures: \(\theta_{E1}\) [K] | 53.6(7) | 3       |
| \(\theta_{E2}\) [K] | 158(2) | 9       |
| \(\theta_{E3}\) [K] | 270(13) | 4       |
| \(\theta_{E4}\) [K] | 314(7) | 8       |
| Anharmonic coefficient \(\alpha\) [1/K] | 1.37(15) \(10^{-4}\) |         |

while \(\theta_D\) is a paramagnetic Curie temperature. The least squares fitting of the experimental data gave values of the effective magnetic moments and the paramagnetic Curie temperatures which are listed in Table 2. The values of \(\mu_{eff}\) are close to those predicted for free \(R^3^+\) ions. The paramagnetic Curie temperatures, except the one for \(R = \text{Pr}\), are negative, indicating dominant character of antiferromagnetic interactions. This result is in agreement with the maxima observed at low temperatures in the temperature dependence of magnetic susceptibility (see insets in Fig. 2a–i), which are typical of antiferromagnetic transitions. The Néel temperatures determined from the measurements are listed in Table 2. For the Tb-based compounds an additional small intensity maximum, related to the Tb2O3 impurity phase, is visible at 2.4 K. For \(R = \text{Nd}\), a jump at \(T = 4\) K indicates the presence of an additional magnetic phase transition. Hysteresis loops taken at 1.9 K confirm antiferromagnetic properties and show a metamagnetic phase transition. The values of the critical fields connected with the metamagnetic phase transition are listed in Table 2.

3.2. Specific heat data

Fig. 3 presents the temperature dependence of the \(C_p\) for the Nd2PdGe6 specific heat in the temperature range of 2–114 K. A high temperature part of the specific heat dependence, i.e. the one above 15.5 K, was analyzed in terms of the following formula:

\[
C_p = C_p^{\text{ph+ed}} = \frac{9\gamma R}{1 - \alpha T} \left( \frac{T}{\theta_D} \right)^{\frac{3}{2}} \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx + \frac{R}{1 - \alpha T} \sum_{i=1}^4 m_i \left( \frac{\theta_{Ei}}{T} \right)^2 \exp \left( \frac{\theta_{Ei}}{T} - 1 \right)
\]

where \(\theta_D\) is a Debye temperature, \(\theta_{Ei}\) are Einstein temperatures and \(m_i\) are corresponding multiplicities for each individual optical branch. \(\alpha\) stands for an anharmonic coefficient and \(R\) is the gas constant. The electronic contribution to the specific heat – usually introduced as \(\gamma T\), where \(\gamma\) is an electronic specific heat (Sommerfeld) coefficient – is omitted as the values of \(\gamma\) reported for the isostructural R3PdGe6 compounds are small: 3.6 mJ/(mol·K²) \((R = \text{La})\) [6] and 14 mJ/(mol·K²) \((R = \text{Ce})\) [19] and therefore this term can be neglected at higher temperatures where the phononic contribution is dominant. With nine atoms per molecule of Nd3PdGe6, there are in total 3x9 = 27 phonon modes: 3 acoustic and 24 optical ones. In order to facilitate analysis, the summation over 24 independent optical branches was grouped into 4 branches with the 3, 9, 4, 8-fold multiplicities. A fit to the experimental data (denoted in Fig. 3 by a red solid line) was performed from 15.5 K to 114 K, i.e. far above the peaks observed at low temperatures. The corresponding fit parameters are gathered in Table 3.

The low temperature data of the Nd3PdGe6 specific heat reveal a complex behavior with a sharp maximum at \(T = 4\) K (see also the \(C_m/T\) data in the inset of Fig. 3) hinting at its first order character. This is in
Fig. 4. Neutron diffraction patterns of a) Pr$_2$PdGe$_6$ at 2.0 and 13.4 K, b) Nd$_2$PdGe$_6$ at 1.9, 4.0 and 6.8 K, c) Tb$_2$PdGe$_6$ at 1.9 and 60.4 K, d) Dy$_2$PdGe$_6$ at 1.9 and 39.7 K, e) Ho$_2$PdGe$_6$ at 1.9 and 13 K, f) Tb$_2$PtGe$_6$ at 1.9 and 55.3 K and g) Er$_2$PtGe$_6$ at 1.9 and 5.9 K. The squares represent the experimental points. The solid lines indicate the calculated profile of the crystal structure and the difference between the obtained and calculated intensity (in the bottom of the diagram). The vertical bars indicate the positions of Bragg reflections: nuclear (first row) and magnetic (second row) ones. The diffraction patterns of Ho$_2$PdGe$_6$ (the inset e) contain a small contribution originating from HoPd$_{0.22}$Ge$_2$. The third and fourth rows of the vertical bars refer to the nuclear and magnetic contributions arising from HoPd$_{0.22}$Ge$_2$. 
agreement with the DC magnetic data (see the inset in Fig. 2b). With increasing temperature a small maximum at $T = 4.2$ K followed by a broad one at $T = 5.6$ K with a quick decrease at 6 K are observed. These anomalies correlate with a small maximum in the magnetic susceptibility visible at 6.5 K (see Fig. 2b).

The Nd$^{3+}$ ions occupy the 16 g crystallographic position in the crystal unit cell of Nd$_2$PdGe$_6$. The crystal field potential of the symmetry related to the 16 g Wyckoff site splits the neodymium $^4I_{9/2}$ ground multiplet into five doublets. The temperature variation of the magnetic entropy $S_m(T)$ derived from the $C_m/T$ dependence (see the inset in Fig. 3) exhibits a distinct change in slope at the Néel temperature. $S_m(T)$ above $T_N$ reaches the value of 9.64 J/(mol K$^2$) which is in reasonable agreement with the theoretical one of 2Rln2 = 11.53 J/ (mol K$^2$) expected for the doublet ground state of 2Ni, Nd$^{3+}$ ions within one mole of Nd$_2$PdGe$_6$ ($N_A$ is the Avogadro number). A discrepancy between these two numbers can be attributed to a systematic error related to the estimation of the phononic contribution to the specific heat which was subtracted from the experimental data in order to obtain the pure magnetic contribution.

### 3.3. Neutron diffraction data

#### 3.3.1. Crystal structure

The neutron diffraction patterns in the paramagnetic state, collected above the respective Néel temperatures (see Fig. 4a-g), confirm that all samples have an orthorhombic crystal structure of the Yb$_2$PdGe$_6$-type [3]. In the unit cell of this structure the atoms occupy the following positions: the R and Ge1 atoms at the 16 g sites: (x, y, z) while the Pd or Pt atoms as well as Ge2, Ge3, Ge4 and Ge5 atoms at the 8f sites: (0, y, z) with different values of $x_i$, $y_i$, and $z_i$ for each corresponding atom. The values of the lattice parameters and atomic positional parameters determined here are listed in Table 3. This type of a crystal structure is characterized by a sequence of atomic planes stacked along a much elongated c-axis ($c/(a,b) \sim 2.65$) with the values of a and b lattice parameters very close one to another ($a/b \sim 1.015$) resulting in a layered structure with large distances between the magnetic rare-earth atoms (see Fig. 5).

#### 3.3.2. Magnetic structure

All the neutron diffraction patterns collected for the samples below their respective Néel temperatures contain a large number of additional peaks of the magnetic origin (see Fig. 4a-g) which can be indexed within a magnetic unit cell identical with the crystal one, suggesting that the magnetic structure is a commensurate one with the propagation vector $k = [0, 0, 0]$. A high-intensity peak at $2\theta = 6.3'$ observed for R$_2$PdGe$_6$ (R = Pr, Nd) and indexed as (001) as well as the one at $2\theta = 12.7'$ indexed as (002) and found for all the other compounds imply that the magnetic moments lay in the basal a-b plane. The 16 rare-earth atoms in the unit cell occupy the 16 g Wyckoff site (with coordinates of particular rare earth atoms listed in Table 5). In order to determine magnetic structures, a symmetry analysis has been performed for the R moments occupying the 16 g Wyckoff site. The package computer program, which is distributed together with FullProf [24], was utilized for the symmetry analysis. Naming of the rare earth ions positions as well as irreducible representations follows the nomenclature introduced by Qi et al. [15]. The full symmetry analysis is presented in Table 1 in Ref. [15]. In this work only the magnetic structure models that fit the experimental data are described in details. In the text below, the u parameter refers to the x-component of the Fourier coefficient of the magnetic moment, and the v parameter to the y-component thereof.

The magnetic order in Pr$_2$PdGe$_6$ is found to be a non-collinear antiferromagnetic one with magnetic moments consisting of the components along the a- and b-axes, related to the $\Gamma_a(u)$ and $\Gamma_a(v)$ models, respectively (see Table 5). The a-axis component of the Pr magnetic moment is equal to 1.42(8) $\mu_B$ while the b-axis one to 2.43(3) $\mu_B$, resulting in a total moment of 2.85(5) $\mu_B$ at 2.0 K ($R_{magn} = 9.2\%$). This order is stable up to the Néel temperature of 13 K.

A similar magnetic structure model is found in Nd$_2$PdGe$_6$ except that only the b-axis magnetic moment component, related to $\Gamma_b(v)$, is present (see Fig. 6b). This magnetic order is stable within the temperature range 1.5 K–3.5 K. The Nd magnetic moment equals 2.11(2) $\mu_B$ at 1.5 K ($R_{magn} = 7.3\%$). A transition to a modulated magnetic structure related to the propagation vector $k = [0.333, 0.27, 0]$ takes place around 4 K (see Fig. 6c).

The powder diffraction patterns of R$_2$PdGe$_6$ (R = Tb, Dy and Ho) and Tb$_2$PtGe$_6$ collected at low temperatures show similar distribution of
magnetic re
efl
ctions. A detailed analysis of the magnetic contribution to
the patterns indicate that:

– the high-intensity reflections correspond to the magnetic order re-
related to the $\Gamma_6(v)$ model (see Table 4) with magnetic moments along
the b-axis and magnitudes of 8.32(7), 7.04(8), 7.42(7) and
8.50(5) μB, respectively,
– the low-intensity reflections correspond to the magnetic order re-
related to the $\Gamma_6(u)$ model with magnetic moments along the a-axis
and magnitudes of 2.29(7), 3.39(7), 3.39(3) and 2.27(7) μB, re-
spectively.

As a result, a non-collinear magnetic structure is developed (see
Fig. 6d) with the total magnetic moments equal to 8.64(7), 7.80(8),
8.39(7) and 8.86(6) μB, respectively, and the corresponding values of
the $R_{\text{magn}}$ factor of 5.4, 8.6, 6.4 and 2.7%. This order is stable up to the
Néel temperature.

Different distribution of the peaks of the magnetic origin is ob-
served in Er$_2$PtGe$_6$. The Bragg re
efl
ctions of the magnetic origin can be
indexed in the magnetic unit cell identical with the crystal one (k = [0,
0, 0]). Analysis of the intensity of magnetic re
efl
ctions shows that the
magnetic ordering of Er moments corresponds to the
$\Gamma_6(u)$ model (see
Table 5) with the moment equal to 7.58(9) μB (at 1.9 K) and parallel to
the a-axis (see Fig. 6e) ($R_{\text{magn}} = 6.9\%$). This order is stable up to the
Néel temperature.

The values of the magnetic moments derived from neutron diffrac-
tion data are listed in Table 2.

3.3.3. Temperature dependence of the parameters of the crystal and
magnetic structures

For all the compounds the neutron diffrac-
tion patterns have been
collected as a function of temperature. Based on these data, the tem-
perature dependences of the a, b, c lattice parameters, unit cell volume
and values of the magnetic moments have been determined and are
presented in Fig. 7. In all of the compounds, except Nd$_2$PdGe$_6$, the low
temperature magnetic structures are stable up to the respective Néel
temperatures. The transition between the antiferro- and paramagnetic
states is associated with a jump in the lattice parameters and unit cell
volume. In the case of Nd$_2$PdGe$_6$, this effect is found only for the
transition between the commensurate collinear antiferromagnetic or-
dering and the incommensurate modulated one which takes place
around 4 K. For this compound no further change in lattice parameters
and unit cell volume is detected at the Néel temperature. The numerical
values of the changes in the lattice parameters and unit cell volume
together with the magnetic moments derived from neutron diffraction
data are summarized in Table 6. One can find that the jumps in the
lattice parameters are relatively large for the R$_2$PtGe$_6$ compounds.

4. Discussion

The results of the X-ray and neutron diffrac-
tion measurements
presented in this work confirm that the investigated compounds have
an orthorhombic crystal structure of the Yb$_2$PdGe$_6$-type. Magnetic
measurements and neutron diffrac-
tion data indicate that the com-
ounds are antiferromagnets with the magnetic moments localized on
the rare-earth atoms. The determined values of the effective magnetic
moments are close to those predicted for free R$^{3+}$ ions while the
magnetic moments in the ordered state, as found from magnetization as
well as from the neutron diffraction data, are smaller than those of free
R$^{3+}$ ions.

The layered magnetic structures determined for the R$_2$TGe$_6$
(T = Pd, Pt) compounds are characterized by a ferromagnetic or nearly
ferromagnetic arrangement of the R moments within the (001) plane
and two different sequences of the moments in the neighboring planes,

Fig. 6. Magnetic structures of a) Pr$_2$PdGe$_6$, b) Nd$_2$PdGe$_6$ (the low temperature
phase), c) Nd$_2$PdGe$_6$ (the high temperature phase), d) R$_2$PdGe$_6$ (R = Tb, Dy
Ho) and Tb$_2$PtGe$_6$, and e) Er$_2$PdGe$_6$. magnetic reflections. A detailed analysis of the magnetic contribution to
the patterns indicate that:
In Er$_2$PdGe$_6$ the magnetic moments are parallel to the a-axis as found for Pr$_2$PdGe$_6$, ~15° for Tb$_2$TGe$_6$ and ~25° for Dy$_2$PdGe$_6$ and Ho$_2$PdGe$_6$.

The magnetic moments form an angle with the (001) plane with components along the a- and b-axes is observed.

For R = Nd and Er, and a non-collinear one for R = Pr, Tb, Dy, Ho. The non-collinear order is different from that observed in the R$_2$TGe$_6$ compounds [12-15]. Another difference is detected between the magnetic structures of Nd$_2$NiGe$_6$ and Nd$_2$PdGe$_6$: in the first compound the magnetic order is stable in the entire temperature range up to the Néel temperature, while in the second one a change of the magnetic order is connected with the change of the sign of the Stevens operator $\alpha_R$ due to a change of the local symmetry of the rare earth atoms. However, the macroscopic parameters, like the Néel temperatures, critical magnetic fields, and paramagnetic Curie temperatures, are not much affected (compare the data in Table 1 in Ref.[13] to those in Table 2 in this work). On the contrary, a change in the local symmetry of the rare earth atoms results in a doubling of the a and b lattice parameters for the second group as well as in a change of the local magnetic moments.

In Gd$_2$PdGe$_6$, the magnetic moments parallel to the a-axis as found in the ErNi$_5$Ge$_6$. A drastic change of the direction of magnetic moments between the Tb-, Dy-, Ho- and Er-based compounds is connected with the change of the sign of the Stevens operator $\alpha_R$ from negative (Tb, Dy, Ho) to positive (Er).

Table 5

| Atom position | $\Gamma_1(\alpha)$ | $\Gamma_2(\alpha)$ | $\Gamma_3(\alpha)$ | $\Gamma_4(\alpha)$ | $\Gamma_5(\alpha)$ |
|---------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| S1 (x, y, z)  | +                 | +                 | +                 | +                 | +                 |
| S2 (-x, -y+1/2, z+1/2) | -                 | -                 | +                 | +                 | +                 |
| S3 (-x, y+1/2, -z+1/2) | +                 | +                 | -                 | +                 | +                 |
| S4 (x, -y, z) | +                 | +                 | +                 | +                 | +                 |
| S5 (-x, -y, -z) | +                 | +                 | +                 | +                 | +                 |
| S6 (x, y+1/2, -z+1/2) | -                 | -                 | +                 | +                 | +                 |
| S7 (-x, -y+1/2, z+1/2) | +                 | +                 | -                 | +                 | +                 |
| S8 (-x, -y, x) | +                 | +                 | -                 | -                 | +                 |

The lattice parameters a, b, and c, unit cell volume V and positional atoms parameters xi, yi, zi for R$_2$TGe$_6$ (R = Pr, Nd, Tb, Dy, Ho, Er; T = Pd, Pt) obtained from the neutron diffraction data in the paramagnetic state.

Table 4

| Parameter | Pr$_2$PdGe$_6$ | Nd$_2$PdGe$_6$ | Tb$_2$PdGe$_6$ | Dy$_2$PdGe$_6$ | Ho$_2$PdGe$_6$ | Tb$_2$PtGe$_6$ | Er$_2$PtGe$_6$ |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| T [K]     | 13.4 K         | 6.8 K          | 45 K           | 39.7 K         | 13 K           | 55.3 K         | 5.9 K          |
| a [Å]     | 8.3279(16)     | 8.3099(12)     | 8.1861(18)     | 8.1604(16)     | 8.1502(13)     | 8.1383(11)     | 8.0925(16)     |
| b [Å]     | 8.1717(15)     | 8.1588(12)     | 8.0548(16)     | 8.0363(14)     | 8.0377(12)     | 8.0475(10)     | 8.0193(16)     |
| c [Å]     | 22.0676(39)    | 21.9646(31)    | 21.6022(50)    | 21.5331(44)    | 21.5096(37)    | 21.7086(27)    | 21.6146(44)    |
| V [Å$^3$] | 1501.28(48)    | 1491.33(37)    | 1424.39(53)    | 1412.13(48)    | 1408.38(39)    | 1421.77(31)    | 1402.71(48)    |

Fig. 8 shows the experimentally determined values of the Néel (T$_N$) and paramagnetic Curie ($\theta_p$) temperatures for R$_2$TGe$_6$ (T = Ni, Pd) as a function of the de Gennes factor. The linear dependence, predicted by the RKKY theory, is represented by the solid lines which are normalized with respect to the data obtained by the respective Gd-based compounds. The theoretical de Gennes scaling is fulfilled for a majority of the investigated compounds, confirming the indirect exchange interactions of the RKKY-type. This result is in agreement with the large R-R interatomic distances and metallic character of the temperature dependence of the electrical resistivity [21]. Noticeable discrepancy between the experimental and theoretical values of T$_N$ for Tb$_2$TGe$_6$ (T = Ni, Pd) can be attributed to the influence of the crystalline electric field [26]. The role of the CEF manifests itself also in a reduction of the magnetic moments in the ordered state in comparison to the free R$^{3+}$ ion values (see Table 2).

The presented data are in agreement with the magnetic data collected for single crystals [21] indicating:

- a collinear AF ordering with the Gd moments along b-axis in Gd$_2$PdGe$_6$,
- the b-axis being a hard magnetic direction and the magnetic moments located in the a-b plane in Tb$_2$PdGe$_6$ (the results based on the temperature dependence of magnetoresistance).

Both the previously reported R$_2$TGe$_6$ (T = Ni, Cu; R = Tb, Ho and Er) [13] as well as the R$_2$PdGe$_6$ (R = Pr, Nd, Gd-Er) and R$_2$PtGe$_6$ (R = Tb, Ho, Er) presented in this work have an orthonhombic layered crystal structure which is related to the Ammt2 space group for the first group of compounds and to Cmca for the second one. A change in the space group results in a doubling of the a and b lattice parameters for the second group as well as in a change of the local symmetry of the rare earth atoms. However, the macroscopic parameters, like the Néel and paramagnetic Curie temperatures, effective magnetic moments and critical magnetic fields are not much affected (compare the data in Table 1 in Ref. [13] to those in Table 2 in this work).

On the contrary, the change in the local symmetry and the corresponding modification of the CEF parameters influences the microscopic magnetic order, i.e. collinear magnetic structures are favored in R$_2$TGe$_6$ (T = Ni, Cu; R = Tb, Ho and Er) [13] while non-collinear ones are favored in R$_2$PdGe$_6$ (R = Pr, Nd, Gd-Er) and R$_2$PtGe$_6$ (R = Tb, Ho, Er).
Fig. 7. Temperature dependence of the $a$, $b$ and $c$ lattice parameters together with the unit cell volume $V$ and the values of the magnetic moments $\mu$ in a) Pr$_2$PdGe$_6$, b) Nd$_2$PdGe$_6$, c) Tb$_2$PdGe$_6$, d) Dy$_2$PdGe$_6$, e) Ho$_2$PdGe$_6$, f) Tb$_2$PtGe$_6$ and g) Er$_2$PtGe$_6$. The Néel temperature is marked by the black triangle at the bottom of each figure.
calculated values are normalized to the experimentally observed temperatures for the respective Nd$_2$PdGe$_6$ compounds. o and p indicate the magnetically ordered and paramagnetic states, respectively, as derived from neutron diffraction. In the case of Nd$_2$PdGe$_6$, the data refer to the transition between the commensurate and incommensurate magnetic structures.

Table 6

| Compound | $\Delta a$ [Å] | $\Delta b$ [Å] | $\Delta c$ [Å] | $\Delta V$ [Å$^3$] |
|----------|----------------|----------------|----------------|-------------------|
| Pr$_2$PdGe$_6$ | 0.0086 | 0.0072 | 0.0188 | 4.22 |
| Nd$_2$PdGe$_6$ | 0.008 | 0.0075 | 0.0188 | 3.88 |
| Tb$_2$PdGe$_6$ | 0.010 | 0.0035 | 0.007 | 3.00 |
| Dy$_2$PdGe$_6$ | 0.0045 | 0.002 | 0.003 | 1.30 |
| Ho$_2$PdGe$_6$ | 0.0085 | 0.0075 | 0.03 | 4.13 |
| Tb$_2$PtGe$_6$ | 0.015 | 0.0125 | 0.025 | 7.0 |
| Er$_2$PtGe$_6$ | 0.011 | 0.011 | 0.025 | 5.6 |

Fig. 8. The Néel and paramagnetic Curie temperatures vs. de Gennes factor $(gJ - 1)\sqrt{(J + 1)}$ for the R$_2$PdGe$_6$ and R$_2$NiGe$_6$ compounds. The solid lines represent the theoretical dependence predicted by the RKKY theory. The calculated values are normalized to the experimentally observed temperatures for the respective Gd-based compounds.

5. Summary

The results presented in this work confirm that the ternary R$_2$TGe$_6$ (R = Pr, Nd, Gd; T = Pd, Pt) compounds crystallize in the orthorhombic Yb$_2$PdGe$_6$-type structure (space group Cmca). The magnetic and neutron diffraction data indicate that the magnetic properties in these compounds are derived from the well localized 4fn-electrons of the rare earth atoms. In all of the compounds the rare earth moments order antiferromagnetically at low temperatures and form collinear magnetic structures in Nd$_2$PdGe$_6$ and Er$_2$PtGe$_6$ and non-collinear ones in R$_2$PdGe$_6$ (R = Pr, Tb-Ho) and Tb$_2$PtGe$_6$. The observed magnetic structures result from a competition between the exchange interactions and crystalline electric field.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Boguslaw Penc: Formal analysis, Visualization. Stanislaw Baran: Formal analysis, Investigation, Writing - review & editing, Visualization. Andreas Hoser: Investigation. Janusz Przewoźnik: Formal analysis, Investigation, Formal analysis, Writing - original draft, Visualization. Andrzej Szytula: Investigation, Writing - review & editing.

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