Crystal structure and complex magnetic properties of R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} compounds (R = Y, Gd–Er)

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Magnetic properties of the R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} compounds (R = Y, Gd–Er) were investigated by means of X-ray diffraction and magnetic measurements. Three of these compounds, namely those with R = Y, Ho and Er, are newly synthesized. The compounds crystallize in the orthorhombic Nd\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9}-type crystal structure (oC\textsubscript{4}h8, C\textsubscript{mmm}) in which the rare earth atoms occupy five nonequivalent sublattices. Magnetic properties of the investigated compounds are related mainly to the R\textsuperscript{3+} ions, except the case of Y\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9} which is a Pauli paramagnet. For R = Gd–Er, the values of effective magnetic moments in the paramagnetic state are close to the free R\textsuperscript{3+} ion values while the moments in the ordered state at T = 2 K and H = 90 kOe are lower than the respective R\textsuperscript{3+} moments. The compounds have complex magnetic properties. All paramagnetic Curie temperatures are positive suggesting that the ferromagnetic interactions are predominant. However, the low temperature data indicate an antiferromagnetic order. With increase of temperature the magnetic properties change from antiferro- to ferrimagnetic and finally to paramagnetic ones. The critical temperatures of magnetic ordering do not fulfill the de Gennes scaling, indicating a crystalline electric field contribution to stabilization of the magnetic order at low temperatures. The neutron diffraction measurements, performed for Ho\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9}, reveal a coexistence of two magnetic phases at low temperatures: the antiferromagnetic with propagation vector \( k = [0,0,\frac{1}{2}] \) and the ferrimagnetic one with \( k = [0,0,0] \). The antiferromagnetic order is predominant at low temperatures while the ferrimagnetic one dominates at intermediate temperatures.

\section{1. Introduction}

The rare-earth—transition metal—In (R-T-In) ternary systems form a rich group of the intermetallic compounds with interesting crystal structure and unique physical properties [1]. In recent years the isostructural R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} compounds (Nd\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9}-type structure, Pearson symbol oC\textsubscript{4}h8, space group C\textsubscript{mmm}) were intensively investigated. According to magnetic measurements they exhibit complex magnetic properties at low temperatures with multiple magnetic transitions [2–6]. Investigation of the fibrous samples of R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} (R = Gd, Tb, Dy and Ho) revealed strong magnetic anisotropy with easy magnetization along the c-axis [4–6]. Neutron diffraction data for R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} (R = Tb and Ho) showed that magnetic moments in different sublattices order at different temperatures [6].

During investigation of the R-Pd-In system at 870 K an existence of the R\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9} (R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy) compounds [7] with the Nd\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9}-type structure [8] has been established. The compounds have complex crystal structure in which the rare earth atoms occupy five nonequivalent crystallographic positions.

Among the R\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9} compounds, their magnetic properties have already been determined only for Ce\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9}, which is a ferromagnet below \( T_c = 18.6 \) K with additional order-order magnetic transition at \( T_t = 1.6 \) K [9].

This work is a part of our investigation of magnetic properties of ternary rare-earth—transition metal indides, in purpose to determine the influence of different factors, like: composition, crystal structure and chemical bonding, on magnetic properties of these compounds. In the previous work we have concentrated on the compounds with T = Ni [2, 3,10]. In this work we report the results of X-ray diffraction and dc magnetic measurements of the R\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9} (R = Y, Gd–Er) compounds. From these data, the crystal structure parameters at room temperature as well as magnetic properties within the temperature range between 1.9
Fig. 1. X-ray diffraction pattern (CuK$_\alpha$ radiation) of Ho$_{11}$Pd$_4$In$_9$ collected at room temperature. The solid circles are for the experimental data, the line shows the result of Rietveld refinement, the vertical bars mark the Bragg reflection positions while the difference between the experimental data and the refinement is plotted at the bottom of the figure.

Fig. 2. Projection of the Ho$_{11}$Pd$_4$In$_9$ crystal structure onto the xy plane and coordination polyhedra of atoms.
and 390 K and external magnetic fields (up to 90 kOe) are determined.

In order to explain the complex magnetic properties of Ho11Pd4In9, additional neutron diffraction measurements at low temperatures were performed.

### Table 1

Crystallographic data obtained from Rietveld refinement, based on the X-ray powder diffraction patterns collected at room temperature for R11Pd4In9 (Nd11Pd4In9-type structure, space group Cmmm).

| R     | Y    | Gd    | Tb   | Dy   | Ho   | Er   |
|-------|------|-------|------|------|------|------|
| M [g/mole] | 2437.01 | 3188.79 | 3207.22 | 3246.54 | 3273.27 | 3298.89 |
| a [Å]     | 14.515(3) | 14.606(2) | 14.540(2) | 14.489(3) | 14.450(2) | 14.420(2) |
| b [Å]     | 21.853(3) | 21.985(3) | 21.872(3) | 21.802(4) | 21.743(3) | 21.710(3) |
| c [Å]     | 3.6535(6) | 3.6997(9) | 3.6737(9) | 3.6455(10) | 3.6326(4) | 3.6138(4) |
| V [Å³]    | 1158.9(5) | 1188.1(4) | 1168.3(3) | 1151.6(5) | 1141.3(2) | 1131.6(3) |
| R1 at 8p (x, y, 0) | x = 0.240(1) | 0.238(7) | 0.239(7) | 0.240(1) | 0.240(8) | 0.241(2) |
| R2 at 4i (0, y, 0) | y = 0.174(1) | 0.172(6) | 0.172(6) | 0.171(1) | 0.170(4) | 0.172(1) |
| R3 at 4i (0, y, 0) | y = 0.372(1) | 0.373(7) | 0.372(7) | 0.371(1) | 0.370(5) | 0.372(2) |
| R4 at 4q (x, 0, 0) | x = 0.303(2) | 0.309(8) | 0.308(10) | 0.308(2) | 0.305(12) | 0.301(2) |
| R5 at 2a (0, 0, 0) | Pd at 8q (x, y, ½) | x = 0.345(1) | 0.344(9) | 0.345(9) | 0.344(2) | 0.345(8) | 0.344(2) |
| In1 at 8q (x, y, ½) | x = 0.105(1) | 0.102(7) | 0.102(7) | 0.101(1) | 0.101(7) | 0.102(2) |
| In2 at 8q (x, y, ½) | y = 0.263(1) | 0.261(5) | 0.261(5) | 0.261(1) | 0.262(4) | 0.262(2) |
| In3 at 2c (½, 0, ½) | y = 0.072(1) | 0.073(5) | 0.073(5) | 0.073(1) | 0.071(4) | 0.072(1) |
| Bo | 1.2(2) | 1.2(2) | 1.4(2) | 0.9(3) | 1.9(2) | 1.8(1) |
| G1 texture parameter | 0.09(3) | 0.90(2) | 0.88(2) | 0.55(3) | 0.28(2) | 0.04(3) |
| R | 0.08 | 0.78 | 0.766 | 0.52 | 2.71 | 6.24 |
| R aniso | 5.43 | 7.79 | 6.81 | 6.35 | 4.42 | 6.61 |

*R The G1 parameter of the original Rietveld preferred orientation function (NOR = 0).*

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### Fig. 3.

(a) Lattice parameters a, b and c along with the unit cell volume V for the R11T4In9 (T = Ni, Pd) compounds as a function of r(R3+) - the effective ionic radius of heavy rare-earths with coordination number VI. The filled triangle symbols refer to the experimental data for R11Pd4In9 as presented in this work while the open ones - to the literature data from Ref. [7]. The open circles refer to the R11Ni4In9 series accordingly to the literature data from Refs. [2,3,5,10]. (b) Relative changes in the lattice parameters of R11T4In9 (T = Ni, Pd) as a function of r(R3+). Δa = [(a(Pd)-a(Ni))/a(Ni)] × 100%, etc. The radii were taken from Ref. [12].

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2. **Experiment**

The samples of R11Pd4In9 were prepared by arc-melting of high purity metals (99.9 wt% purity for R, 99.99 wt% for Pd and In) having total mass of 1.5 g under a pure argon atmosphere. The buttons were sealed in evacuated silica tubes and annealed at 870 K for one month. The
powdered polycrystalline samples were measured at room temperature using a PANalytical X’Pert PRO diffractometer (Cu Kα-radiation, Bragg-Brentano geometry, measured angle interval 2θ = 10-180°, step scan mode, step size in 2θ = 0.026°, 480 s/step). The FullProf [11] program package was used for X-ray phase and Rietveld analysis of the collected data set.

The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform. Three types of magnetic measurements were performed: collecting ZFC (zero field cooling) and FC (field cooling) magnetic susceptibility curves in applied field of H = 90 kOe from 1.9 to 390 K (in order to determine phase transition temperatures), then scanning from 1.9 K up to 390 K in magnetic field of 1 kOe (in order to determine the effective magnetic moment μ_eff and paramagnetic Curie temperature θ_p).

Table 2
Magnetic properties of R11Pd4In9 (R = Gd–Er): the Curie and transitions temperature (T_c, T_t), the paramagnetic Curie temperature (θ_p), experimental (exp.) and theoretical (theor.) values of the effective magnetic moment (μ_eff) and of the moment in the ordered state (μ) at T = 1.9 K (or 2.0 K for Tb11Pd4In9) and H = 90 kOe together with the theoretical value for free R^{3+} ion.

| R  | T_c [K] | T_t [K] | θ_p [K] | μ_eff [μB] | μ [μB] |
|----|---------|---------|---------|-------------|--------|
|    | exp.    | theor.  | exp.    | theor.      |        |
| Gd | 66      | 23      | 37      | 8.09        | 7.94   |
| Tb | 106     | 78      | 24      | 9.70        | 9.72   |
| Dy | 88      | 70      | 11.2    | 10.64       | 10.65  |
| Ho | 18.7    | 8.4     | 3.0     | 10.73       | 10.61  |
| Er | 19.6    | 7.0     | 1.1     | 9.72        | 9.59   |
and finally measuring magnetization curves and hysteresis loops up to 90 kOe at selected temperatures.

For the polycrystalline sample of Ho$_{11}$Pd$_4$In$_9$ additional powder neutron diffraction measurements with the use of the E6 diffractometer installed at the BERII reactor (BENS, Helmholtz-Zentrum Berlin) were performed. The incident neutron wavelength was $\lambda = 2.432$ Å while temperature ranged from 1.5 up to 24.6 K. The Rietveld-type program FullProf [11] was used for processing the data.

3. Results

3.1. Crystal structure

X-ray powder diffraction data collected at room temperature for the R$_{11}$Pd$_4$In$_9$ samples indicate (Fig. 1 shows exemplary data for Ho$_{11}$Pd$_4$In$_9$) that the investigated compounds crystallize in the Nd$_{11}$Pd$_4$In$_9$-type crystal structure (Pearson symbol oC48, space group Cmmm) [8]. Fig. 2 shows the projection of the atoms on the $xy$ plane for Ho$_{11}$Pd$_4$In$_9$ and illustrates the coordination polyhedra of all the atoms, viz. [Ho$_1$Pd$_2$In$_6$Ho$_6$], [Ho$_2$In$_8$Ho$_5$], [Ho$_3$Pd$_4$In$_6$Ho$_6$], [Ho$_5$In$_8$Ho$_4$], [PdHo$_6$In$_3$], [In$_1$Pd$_3$Ho$_4$], [In$_2$Pd$_3$Ho$_8$], [In$_4$Pd$_3$Ho$_{11}$].
Fig. 6. Temperature dependence of the Y$_{11}$Pd$_4$In$_9$ magnetic susceptibility taken at H = 1 kOe. The inset shows the magnetization curve at T = 1.9 K.

Table 3
The critical fields for metamagnetic transitions (H$_{cr}$) and coercivity fields (H$_{co}$) in R$_{11}$Pd$_4$In$_9$ (R = Gd–Er) as determined from magnetization vs. applied magnetic field curves. The values in brackets indicate temperatures of measurements.

| R   | H$_{cr}$ [kOe] | H$_{co}$ [kOe] |
|-----|----------------|----------------|
| Gd  | 1.75 (1.9 K), 0.65 (6.0 K), 0.03 (46.0 K) | 1.95 (1.9 K), 1.20 (6.0 K), 0.04 (46.0 K) |
| Tb  | 70 (2.9 K), 25 (13.0 K), 0.7 (43.0 K), 0.06 (95.0 K) | 10.3 (2.0 K), 15.2 (13.0 K), 1.30 (43.0 K), 0.07 (95.0 K) |
| Dy  | 27 (1.9 K and 5.0 K), 34 (14.0 K), 2.3 (35.0 K), 0.07 (81.0 K) | 8.0 (1.9 K), 11.8 (5.0 K), 14.8 (14.0 K), 3.1 (35.0 K), 0.10 (81.0 K) |
| Ho  | 5.6 (1.9 K), 1.90 (5.0 K), 0.20 (15.5 K) | 0.72 (1.9 K), 0.82 (5.0 K), 0.13 (15.5 K) |
| Er  | 1.70 (1.9 K), 0.45 (6.0 K), 0.22 (10.5 K), 0.12 (14.0 K) | 0.96 (1.9 K), 0.23 (6.0 K), 0.10 (10.5 K), 0.05 (14.0 K) |

[In$_3$Pd$_4$Ho$_8$In$_2$]. The Ho atoms, which are situated at five different Wyckoff positions, occupy one layer of the structure (z = 0) while the second one (z = 1/2) is occupied by the palladium and indium atoms. Refined lattice parameters and atomic coordinates are presented in Table 1 and they are in good agreement with the previous results reported in Ref. [7]. The dependence of the lattice parameters a, b and c and the unit cell volume V (Fig. 3a) vs. effective ionic radius [12] is almost linear and agrees with the lanthamide contraction. The novel R$_{11}$Pd$_4$In$_9$ compounds with R = Y, Ho and Er prolong the concerned series.

3.2. Magnetic data

3.2.1. dc magnetic susceptibility

The results of magnetic measurements for the R$_{11}$Pd$_4$In$_9$ compounds (R = Gd–Er) are presented in Fig. 5a–e and 5a-5f and summarized in Table 2. At high temperatures the reciprocal magnetic susceptibilities of all compounds obey the Curie-Weiss law. The paramagnetic Curie temperatures, as determined from these data, are positive, while the values of effective magnetic moments are close to those predicted for the free R$^3+$ ions (see Table 2).

With decrease of temperature a sharp increase of magnetic susceptibility is observed at 66, 106, 88, 18.7 and 19.6 K for R = Gd, Tb, Dy, Ho and Er, respectively (see upper insets in Fig. 4a-e). The above temperatures have been determined from inflection points in the ZFC $\chi(T)$ curves taken at 50 Oe and are listed in Table 2 as corresponding Curie points. Below Curie temperatures large discrepancies between the ZFC and FC curves are observed. Both curves show additional anomalies at lower temperatures, namely, the maxima at 46 K (ZFC) and 34 K (FC) for R = Gd, 95 K (ZFC) and 62 K (FC) for R = Tb, 81 K (ZFC) and 26 K (FC) for R = Dy, 15.4 K (ZFC) and 12.3 K (FC) for R = Ho and 17.3 K (ZFC) and 7.9 K (FC) for R = Er are observed. Further decrease of temperature leads to rapid decrease of susceptibility indicating additional magnetic transition of the order-order type. The corresponding transition temperatures determined from inflection points in the ZFC $\chi(T)$ curves are listed in Table 2.

Deviations from the Curie-Weiss law are observed below 250 K (R = Gd and Tb), 170 K (R = Dy), 60 K (R = Ho) and 40 K (R = Er) indicating existence of short-range magnetic order above corresponding Curie temperatures.

Magnetic susceptibility of Y$_{11}$Pd$_4$In$_9$ (Fig. 6) takes small values (<0.001 emu/mol) over broad temperature range suggesting that Y$_{11}$Pd$_4$In$_9$ is a Pauli paramagnet. This result is in agreement with small magnetic moment (2.5·10$^{-3}$ μB/Y atom) determined from magnetization measured at 1.9 K. The increase of susceptibility below 100 K is probably related to small amount of magnetic atoms present as impurity in yttrium which is of 99.9 wt% purity.

3.2.2. Magnetization

Magnetization curves and hysteresis loops for R$_{11}$Pd$_4$In$_9$ (R = Gd–Er), measured at selected temperatures in external magnetic fields up to 90 kOe (9 T), are presented in Fig. 5a–f with insets showing the low-field range. The data indicate an influence of external magnetic field on the magnetic ground state. The primary curves, taken for the Gd-compound, indicate metamagnetic phase transitions with the critical fields equal to 1.75 kOe (1.9 K), 0.65 kOe (6.0 K) and 0.03 kOe (46.0 K). The above fields have been determined from inflection points in the primary M(H) curves. The hysteresis loops are characterized by the coercivity fields of 1.95, 1.20 and 0.04 kOe for 1.9, 6.0 and 46.0 K, respectively. The magnetization curve and hysteresis loop, measured at 46.0 K, are typical of a soft ferrimagnetic material. The magnetization
Fig. 7. Neutron diffraction patterns of Ho$_{11}$Pd$_4$In$_9$: the difference patterns of (a) (1.5–24.6 K) and (b) (11.7–24.6 K) together with (c) the pattern collected at 24.6 K. The squares represent the experimental points, the solid lines are for the calculated profiles for the crystal and magnetic structure models (as described in the text) and for the difference between the observed and calculated intensities (in the bottom of each diagram). The vertical bars indicate the positions of Bragg reflections related to: (a) AFM (the upper row) and FiM (the bottom row) magnetic phases, (b) FiM phase and (c) crystal structure.
curves do not show saturation at the highest field available, i.e. 90 kOe (9 T). The value of magnetic moment at $T = 1.9$ K and $H = 90$ kOe equals $2.48 \mu_B$/Gd atom.

The primary magnetization curve taken at 2.0 K for Tb$_{11}$Pd$_4$In$_9$ shows a metamagnetic phase transition in form of a jump at 70 kOe while the curves collected at higher temperatures show metamagnetic phase transitions at 25 kOe (13.0 K), 0.7 kOe (43.0 K) and 0.06 kOe (95.0 K). Hysteresis loops with the coercivity fields equal to 10.3 kOe (2.0 K), 15.2 kOe (13.0 K), 1.30 kOe (43.0 K), 0.07 kOe (95.0 K) are observed. The magnetic moment at $T = 2.0$ K and $H = 90$ kOe equals 2.20 $\mu_B$/$Tb$ atom while the moment at $T = 43.0$ K and $H = 90$ kOe reaches 2.76 $\mu_B$/$Tb$ atom.

The primary magnetization curves of Dy$_{11}$Pd$_4$In$_9$, collected at selected temperatures, indicate several metamagnetic transitions, namely, at 27 kOe (1.9 K and 5.0 K), 34 kOe (14.0 K), 2.3 kOe (35.0 K), and 0.07 kOe (81.0 K). The coercivity fields equal 8.0 kOe (1.9 K), 11.8 kOe (5.0 K), 14.8 kOe (14.0 K), 3.1 kOe (35.0 K) and 0.10 kOe (81.0 K). The magnetic moment at $T = 1.9$ K and $H = 90$ kOe equals 4.14 $\mu_B$/Dy atom. Similar value of 4.22 $\mu_B$/Dy atom is found at $T = 14.0$ K and $H = 90$ kOe.

It is worth noting that hysteresis loops collected at the lowest temperatures for R$_{11}$Pd$_4$In$_9$ ($R = Tb$ and Dy) show a number of jumps indicating field-induced switching between metastable magnetic orderings.

Different shape of magnetization vs. external magnetic field curves is observed in R$_{11}$Pd$_4$In$_9$ ($R = Ho$, Er). In the ordered state, regardless the temperature, these dependences are similar to those observed for ferromagnetic materials. The critical fields of metamagnetic transitions are low, namely, they equal to 5.6 kOe (1.9 K), 1.90 kOe (5.0 K), 0.20 kOe (15.5 K) in Ho$_{11}$Pd$_4$In$_9$ and 1.70 kOe (1.9 K), 0.45 kOe (6.0 K), 0.22 kOe (10.5 K), 0.12 kOe (14.0 K) in Er$_{11}$Pd$_4$In$_9$. Also the coercivity fields are low: 0.72 kOe (1.9 K), 0.82 kOe (5.0 K), 0.13 kOe (15.5 K) in Ho$_{11}$Pd$_4$In$_9$ and 0.96 kOe (1.9 K), 0.23 kOe (6.0 K), 0.10 kOe (10.5 K), 0.05 kOe (14.0 K) in Er$_{11}$Pd$_4$In$_9$. The magnetic moments at $T = 1.9$ K and $H = 90$ kOe equal 6.89 $\mu_B$ per Ho atom and 5.48 $\mu_B$ per Er atom.

It is worth noting that none of the magnetization curves shows saturation at 90 kOe and the determined magnetic moments per rare earth atoms are smaller than the theoretical values expected for free $R^{3+}$ ions, even at the lowest temperatures.

The values of critical and coercivity fields, as determined from the magnetization vs. applied magnetic field dependences, are summarized in Table 3.

### 3.3. Neutron diffraction data

The results of powder neutron diffraction data for Ho$_{11}$Pd$_4$In$_9$, collected at three selected temperatures (1.5, 11.7 and 24.6 K), are presented in Fig. 7. Analysis of the paramagnetic pattern taken at $T = 24.6$ K confirms the crystal structure of the Nd$_{11}$Pd$_4$In$_9$-type ($R_{\text{Bragg}} = 6.51\%$, $R = 4.71\%$). Additional Bragg reflections of magnetic origin are

![Fig. 8. Temperature dependence of Bragg reflection intensities related to the antiferromagnetic (AFM) phase (stars), ferrimagnetic (FiM) phase (triangles) and crystal structure (circles). Due to reflection overlapping the sums of selected reflections are shown as indicated in the legend.](image-url)
visible in the patterns collected at 1.5 and 11.7 K. These reflections can be divided into two groups: the one related to the propagation vector $k = [0,0,1/2]$ and the second one related to $k = [0,0,0]$.

Analysis of the diffraction pattern at 1.5 K shows that the most intense reflections correspond to the antiferromagnetic structure with magnetic unit cell doubled along the $c$-axis when compared to the crystallographic one ($k = [0,0,1/2]$). The best fit has been obtained for a magnetic structure with all holmium magnetic moments within the crystallographic unit cell coupled ferromagnetically and parallel to the $c$-axis direction while the moments in the neighbouring cells along the $c$-axis point at opposite direction (see Fig. 9a). The exact values of magnetic moments are listed in Table 4, where Ho1, ..., Ho5 refer to atoms located at different Wyckoff sites as specified in Table 1. The holmium moments are significantly smaller than 10 $\mu_B$ expected for a free Ho$^{3+}$ ion.

The small intensity reflections form a second group corresponding to a ferrimagnetic structure with partial compensation of magnetic moments (see Fig. 9b). The magnetic unit cell is identical to the crystallographic one ($k = [0,0,0]$). The holmium magnetic moments within each Wyckoff site are coupled ferrimagnetically, namely:

- the Ho1 moments (8p site) have two components: 1.9(2) $\mu_B$ along the $a$-axis and 2.2(2) $\mu_B$ along the $c$-axis with the total value of 2.9(2) $\mu_B$ (the Ho1 moments are inclined at an angle of about 40$^\circ$ to the $c$-axis),
- the Ho2 and Ho3 (two 4i sites) as well as Ho4 (4g site) moments have only the $c$-axis component equal to 4.5(2), 0.8(2) and 2.2(2) $\mu_B$, respectively,
- the Ho5 atoms have no contribution to the ferrimagnetic component of the magnetic structure, and thus their magnetic moments are fixed to zero in Table 4.

Thermal evolution of the diffraction pattern indicate that two contributions to the magnetic structure, the antiferro- (AFM) ($k = [0,0,1/2]$) and ferrimagnetic (FiM) ($k = [0,0,0]$) ones, have different temperature dependence. Fig. 8 shows the intensity vs. temperature plot for selected Bragg reflections taken as representatives of the antiferro- and ferrimagnetic contributions to the magnetic structure together with those related to the crystal structure. Due to reflection overlapping the respective sums of intensities are shown as indicated in the Fig. 8 legend. Intensities of the AFM-related reflections decrease monotonically with temperature and are found absent in the pattern taken at 11.7 K. The highest rate of decrease is found between 4.2 K and 9.7 K. The intensities of the FiM-related reflections show different behavior, they undergo a rapid increase in the temperature range from 4.2 K to 9.7 K, then remain almost constant up to 11.7 K and finally gradually decrease and reach zero in the vicinity of 20 K.

Presented data indicate a coexistence of the antiferro- and ferrimagnetic orderings within the majority of temperature range of the

**Table 5**

| Atom/CN | $\delta$ [Å] | Atom/CN | $\delta$ [Å] |
|---------|---------------|---------|---------------|
| Ho1 Pd 2x | 2.803 | Ho5 In2 8x | 3.168 |
| In2 2x | 3.151 | Ho2 2x | 3.481 |
| CN − 14 In1 2x | 3.234 | CN − 12 Ho5 2x | 3.633 |
| In1 2x | 3.345 | CN − 9 Ho1 2x | 2.803 |
| Ho1 1x | 3.454 | Pd Ho1 1x | 2.921 |
| Ho2 1x | 3.488 | Ho4 2x | 2.938 |
| Ho1 2x | 3.633 | CN − 9 Ho3 2x | 2.938 |
| Ho4 1x | 3.830 | In2 1x | 2.992 |
| Ho3 1x | 3.851 | In1 1x | 3.044 |
| | | | In3 1x | 3.140 |
| Ho2 | In1 4x | 3.239 |
| In2 4x | 3.366 | In1 1x | 2.996 |
| CN − 13 Ho5 1x | 3.481 | Pd 1x | 3.044 |
| Ho1 2x | 3.488 | CN − 12 Ho1 2x | 3.224 |
| Ho2 2x | 3.633 | Ho2 2x | 3.239 |
| Ho3 1x | 3.830 | In2 1x | 3.327 |
| Ho4 2x | 3.978 | CN − 12 Ho1 2x | 3.151 |
| Ho3 2x | 3.633 | In2 1x | 2.992 |
| Ho1 2x | 3.851 | In2 1x | 3.109 |
| Ho4 2x | 3.978 | CN − 12 Ho1 2x | 3.151 |
| Ho4 4x | 3.345 | In3 2x | 3.168 |
| Ho3 2x | 3.633 | In2 1x | 3.344 |
| Ho1 2x | 3.851 | In2 1x | 3.366 |
| Ho4 2x | 3.633 | In2 1x | 3.363 |
| Ho1 2x | 3.830 | In3 Pd 4x | 3.140 |
| Ho3 2x | 3.978 | CN − 14 Ho3 4x | 3.345 |
| | | | In3 2x | 3.351 |

Fig. 9. The (a) antiferro- (AFM) and (b) ferrimagnetic (FiM) contributions to the magnetic structure of Ho$_{11}$Pd$_4$In$_9$. 

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Fig. 10. The distributions of Ho atoms at different sites in Ho$_{11}$Pd$_4$In$_9$ and Ho-Ho interatomic distances in Å.

Fig. 11. The Curie temperatures ($T_c$) and paramagnetic Curie temperatures ($\theta_p$) vs. de Gennes factor for R$_{11}$T$_4$In$_9$ (R = Gd–Er). The data for T = Ni are taken after Refs. [2,3] while for T = Pd are reported in this work. The straight lines indicate theoretical dependence, predicted by the RKKY theory, with Gd-based compounds taken as reference (see main text for details).
magnetically ordered state. The antiferromagnetic order is predominant at low temperatures while the ferrimagnetic one dominates at intermediate temperatures. Both magnetic phases disappear in the vicinity of the Curie temperature. The thermal evolution of different contributions to the magnetic structure is in agreement with the complex temperature dependence of magnetic susceptibility at low temperatures (see the inset in Fig. 4d).

4. Discussion

The work reports the results of X-ray and neutron powder diffraction and dc magnetic measurements for the R11Pd4In9 (R = Y, Gd–Er) series of compounds. The X-ray diffraction data confirm the orthorhombic crystal structure of the Nd11Pd4In9-type which was originally determined, using single-crystal X-ray diffractometry, for Nd11Pd4In9 [8] and Gd11Ni4In9 [4] and described in detail in Refs. [4,5,7,8,10]. The main determined structural features of the compounds are as follows: 1) the structure consists of two layers alternating along the shortest c-axis (much smaller than both the a- or b-axis), thus the layer of larger R atoms forms nets of tetragons and triangles at z = 0, while the layer of smaller in size (Ni,Pd)/In atoms forms nets of tetragons and pentagons at z = ± ½; 2) the crystal structure is formed by the AlB2 (RNNi2) and CsCl (RIn)-type fragments; 3) the lattice parameters decrease linearly with decreasing effective ionic radius of rare earth (Fig. 3a) due to the lanthanide contraction; 4) polycrystalline samples of the compounds are built from well-defined fibers (or rods) quickly growing along the short c-axis due to the presence of short In-In chemical bonds in the a–b plane. The anisotropy of the crystal structure corresponds with strong anisotropy of the physical properties [5].

The refined lattice parameters and atomic coordinates, presented in Table 1, are in good agreement with the previous results for polycrystalline samples reported in Refs. [7] as well as with the single-crystal data for Gd11Ni4In9 [4]. The lattice parameters of the R11Pd4In9 compounds are only little larger than those for the isostructural R11Ni4In9 intermetallics (see Fig. 3b) leading to similar magnetic properties in these two series of compounds. It is worth noting that the relative changes in the a and b lattice parameters (Δa = [(a(Pd)-a(Ni))/a(Ni)] × 100%, etc.), and accordingly the unit cell volume V, increase with decreasing effective ionic radius of the rare-earth element while the change in the shortest c-parameter rather decreases indicating a significant role of the transition element in the interatomic bonding. The refined interatomic distances and coordination numbers of atoms in Ho11Pd4In9, listed in Table 5, well agree with the single-crystal data for Gd11Ni4In9 [4].

The work reports the interesting magnetic properties of the R11Pd4In9 compounds (R = Y, Gd–Er). Y11Pd4In9 is a Pauli paramagnet while the other compounds (R = Gd–Er) order magnetically at low temperatures. The results of the macroscopic magnetic measurements are summarized in Table 2. The effective magnetic moments determined from high temperature data in the paramagnetic state are very close to the free R3⁺ ion values confirming that magnetic moments in R11Pd4In9 (R = Gd–Er) are localized solely on the rare earth R3⁺ ions. The determined values of the paramagnetic Curie temperatures (θp) are positive indicating predominantly ferromagnetic character of the magnetic interactions. Noticeable deviations of the inverse magnetic susceptibility from the Curie-Weiss behavior, visible above respective Curie temperatures, are characteristic of short-range magnetic order. Temperature dependence of the magnetic susceptibilities (see the upper insets in Fig. 4a–e) and magnetization curves (see Fig. 5a–f) indicate a change of magnetic order from the antiferromagnetic ground state at low temperatures, through ferrimagnetic at intermediate temperatures and finally to paramagnetic state. The critical temperatures of magnetic ordering (Tc) are larger than the corresponding paramagnetic Curie temperatures (θp), indicating a presence of an antiferromagnetic contribution to the predominant ferromagnetic interactions, as expected for the high-temperature ferrimagnetic (FIM) phase. The critical and coercivity fields, determined from the magnetization curves and hysteresis loops, show a significant increase while comparing those of Gd11Pd4In9 (L = 0, purely S state) and Tb11Pd4In9 (L > 0), confirming the influence of crystalline electric field on magnetic properties. Further increase of the number of f electrons of the rare earth element leads to decrease of both the critical and coercivity fields.

The results of neutron diffraction experiment for Ho11Pd4In9 show a presence of the complex temperature dependent magnetic structure at low temperatures. The holmium magnetic moments occupying five different Wyckoff sites are of different magnitudes (or are zero in the case of Ho5 in the FIM structure). The moments are parallel or antiparallel to the c-axis with exception for Ho1 in the FIM phase, whose moments are inclined at an angle of about 40° to the c-axis. Such a complex magnetic structure results from the complex crystal structure in which the rare earth atoms occupy five nonequivalent sites with the similar R-R nearest neighbour interatomic distances within particular site or between sites. The different rare earth sites are characterized by different local site symmetry, namely: m for the 8p site, m2m for the 4i sites, 2mm for the 4g site and mmm for the 2a site. Therefore, the magnetic structure results from competition between exchange interactions and local crystalline electric field.

The most of the Ho magnetic moments in the determined magnetic structures of Ho11Pd4In9 (APM and FIM) are parallel to the c-axis. This result is in agreement with the data for R11Ni4In9 (R = Tb, Dy) where the c-axis was found to be an easy magnetization direction [5]. The magnetic structures in the isostructural R11Ni4In9 (R = Tb, Ho) are complex with a number of temperature induced magnetic transitions and magnetic moments pointing at different directions [6], however, those structures are not the same as the ones reported here for Ho11Pd4In9.

One can expect that such a scenario with a number of temperature- or field-induced magnetic transitions appearing consecutively is probably also realized in other members of the investigated R11Pd4In9 (R = Gd–Er) family of compounds, whose magnetic structures have not yet been resolved. Fig. 10 shows the distributions of the Ho atoms located at different sites. The shortest Ho–Ho distances are marked. In the majority of cases these distances are larger than the sum of atomic radii equal to 3.54 Å. Such a large R-R interatomic distances, found in both series of the R11T4In9 (T = Ni, Pd) isostructural compounds, suggest that the magnetic interactions between the rare earth magnetic moments are predominantly driven by the indirect exchange interactions of the RKKY-type [13]. Fig. 11 shows the experimentally determined Curie temperatures and paramagnetic Curie temperatures plotted against the de Gennes factor. The straight lines indicate theoretical dependence, predicted by the RKKY theory, with Gd-based compounds taken as reference owing to the fact that the Gd3⁺ ion is in the S-state with zero orbital momentum and thus is not influenced by the crystalline electric field. The observed large discrepancy between the experimental and calculated temperatures, especially visible in Tc for R = Tb and Dy, indicates strong influence of the crystalline electric field (CEF) on stability of the magnetic order in both series of compounds [14]. Similar discrepancies, attributed to the influence of CEF, have been observed in RRh4B4 [15] and R2CoGe5 (R = rare earth element) [16].

Comparison of the magnetic data for both series of the isostructural R11T4In9 (T = Ni, Pd) compounds indicates limited influence of the transition element T: Ni (3d) and Pd (4d). For both the series the magnetic moments are localized solely on the rare earth atoms. The Ni and Pd atoms do not possess localized magnetic moments. The compounds with R = Gd, Tb, Dy and T = Ni, Pd as well as two members of the Pd-series, namely, R11Pd4In9 (R = Ho, Er), show similar magnetic properties at low temperatures. With increase of temperature the antiferromagnetic ground state transforms in to the ferrimagnetic structure at Tc, which finally undergoes a transition to the paramagnetic state at Tc. The transition temperatures Tc and Tg are similar in both the series (see Table 1 in Ref. [3] and Table 2 in this work). Ho11Ni4In9 is an exception as it is found purely antiferromagnetic while Er11Ni4In9 is non-existent.
5. Summary

The R\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9} compounds (R = Gd–Er) with the complex crystal structure in which the rare earth atoms occupy five nonequivalent sites present interesting magnetic properties. The magnetic moments, localized solely on the rare earth atoms, show complex magnetic ordering with the antiferromagnetic ground state at low temperatures. Applying temperature or external magnetic field induces a transition to the ferrimagnetic order. The critical temperature of magnetic order \( T_c \), temperature or external magnetic field induces a transition to the magnetic state.

Declarations of competing interest

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

S. Baran: Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. Yu. Tyvanchuk: Formal analysis, Investigation, Writing - original draft, Visualization. B. Penc: Formal analysis, Visualization. Ya. Kalychak: Writing - original draft. A. Hoser: Investigation. A. Szytula: Investigation, Writing - original draft, Writing - review & editing.

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References

[1] Ya Kalychak, V. Zaremba, R. Pöttgen, M. Lukachuk, R. D. Hoffmann, Rare earth – transition metal – intermetallics, ch. 218, in: K.A. Gschneidner Jr., J.-C.G. Bünzli, K. Pecharsky (Eds.), Handbook on the Physics and Chemistry of Rare Earths, 3/4(Elsevier, Amsterdam, 2004, pp. 1-133, 2005.
[2] Yu. Tyvanchuk, S. Baran, R. Duraj, Ya. M. Kalychak, J. Przewoznik, A. Szytula, Crystal structure and magnetic properties of Dy\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9}, J. Alloys Compd. 587 (2014) 573–577, https://doi.org/10.1016/j.jallcom.2013.10.084.
[3] A. Szytula, S. Baran, J. Przewoznik, Yu Tyvanchuk, Ya Kalychak, Magnetic properties and specific heat data of R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} (R = Pr, Nd, Sm, Gd and Tb) compounds, J. Alloys Compd. 601 (2014) 238–244, https://doi.org/10.1016/j.jallcom.2014.02.183.
[4] A. Provino, P. Manfrineti, K.A. Gschneidner Jr., S.K. Dhar, D.L. Schlagel, T. A. Lograsso, G.J. Miller, S. Thimmaiah, H. Wang, A.M. Russell, A. Becker, Ya Mudryk, Self-assembled nano- to micron-size fibers from molten R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} intermetallics, Acta Mater. 73 (2014) 27–36, https://doi.org/10.1016/j.actamat.2014.03.061.
[5] A. Provino, K.A. Gschneidner Jr., S.K. Dhar, C. Ferey, G. Mudryk, P. Manfrineti, D. Pauly, V.K. Pecharsky, The nano-microfibrous R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} intermetallics: new compounds and extraordinary anisotropy in Tb\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} and Dy\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9}, Acta Mater. 91 (2015) 128–140, https://doi.org/10.1016/j.actamat.2015.03.003.
[6] C. Ritter, A. Provino, P. Manfrineti, V.K. Pecharsky, K.A. Gschneidner Jr., S. K. Dhar, Magnetic structures of R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} and R\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} (R = Tb and Ho): strong hierarchy in the temperature dependence of the magnetic ordering in the multiple rare-earth sublattices, J. Phys. Condens. Matter 27 (2015) 476601, https://doi.org/10.1088/0953-8984/27/47/476601.
[7] L. Sojka, M. Demchyna, B. Belan, M. Manyako, Ya Kalychak, New compounds with Nd\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9} structure type in the systems RE-Pd-In (RE = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy), Intermetallics 49 (2014) 14–17, https://doi.org/10.1016/j.intermetal.2014.01.003.
[8] L. Sojka, M. Manyako, R. Černý, M. Ivaný, B. Belan, R. Gladyszhevskiy, Ya Kalychak, Nd\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9} compound – a new member of the homological series based on Al\textsubscript{12}B\textsubscript{7} and Ca\textsubscript{12}C\textsubscript{7} types, Intermetallics 16 (2008) 625–628, https://doi.org/10.1016/j.intermetal.2008.01.001.
[9] D. Das, D. Kaczorowski, Ferromagnetic Kondo lattice behavior in Ce\textsubscript{11}Pd\textsubscript{4}In\textsubscript{9}, J. Magn. Magn Mater. 319 (2009) 315–320, https://doi.org/10.1016/j.jmmm.2008.01.002.
[10] M. Pustovoychenko, Yu Tyvanchuk, I. Hayduk, Ya Kalychak, Crystal structure of the RE\textsubscript{11}Ni\textsubscript{4}In\textsubscript{9} compounds (RE = La, Ce, Pr, Nd, Sm, Gd, Tb and Y), Intermetallics 18 (2010) 920–932, https://doi.org/10.1016/j.intermetal.2010.01.005.
[11] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Phys. B Condens. Matter 192 (1995) 55–69, https://doi.org/10.1016/0921-4526(95)90108-4. Commission on Powder Diffraction (ICDD), Newsletter 26 (2001) 12–19; J. Rodríguez-Carvajal.
[12] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr. A 32 (1976) 751–767, https://doi.org/10.1107/S0567739476011515.
[13] P.G. de Gennes, Interactions indirectes entre couches 4f dans les métaux de terres rares, J. Phys. Radium 23 (1962) 510–521, https://doi.org/10.1051/jphysrad:01962002308-9051001.
[14] D.R. Noakes, G.K. Shenoy, The effect of a crystalline electric field on the magnetic transition temperatures of rare-earth rhodium borides, Phys. Lett. A91 (1982) 35–36, https://doi.org/10.1016/0375-9601(82)90258-4.
[15] B.D. Dunlap, L.N. Hall, F. Behroozi, G.W. Crabtree, D.G. Norteños, Crystal-field effects and the magnetic properties of rare-earth rhodium borides, Phys. Rev. B 29 (1984) 6244–6251, https://doi.org/10.1103/PhysRevB.29.6244.
[16] D.A. Joshi, R. Nagalakshmi, S.K. Dhar, A. Thamizhavel, Anisotropic magnetization studies of R\textsubscript{12}Co\textsubscript{14}Ga\textsubscript{34} single crystals (R = Gd, Tb, Dy, Ho, Er, Tm, Y, and Lu), Phys. Rev. B 77 (2008) 174420, https://doi.org/10.1103/PhysRevB.77.174420.