Strong magnetic coupling in the hexagonal $R_5\text{Pb}_3$ compounds ($R = \text{Gd-Tm}$)

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ABSTRACT

We have synthesized the $R_5\text{Pb}_3$ ($R = \text{Gd-Tm}$) compounds in polycrystalline form and performed neutron scattering and magnetization measurements. For all $R_5\text{Pb}_3$ reported here the Weiss temperatures θ_W are several times smaller than the ordering temperatures T_{ORD} , while the latter are remarkably high (T_{ORD} up to 275 K for $R = \text{Gd}$) compared to other known R - M binaries ($M = \text{Si, Ge, Sn and Sb}$). The magnetic order changes from ferromagnetic (FM) in $R = \text{Gd, Tb}$ to antiferromagnetic (AFM) in $R = \text{Dy-Tm}$. Below T_{ORD} , the magnetization measurements together with neutron powder diffraction show complex magnetic behavior and reveal the existence of up to three additional phase transitions, believed to be a result of large anisotropic exchange and/or crystal electric field effects inducing high anisotropy. The $R_5\text{Pb}_3$ magnetic unit cells for $R = \text{Tb - Tm}$ can be described with incommensurate magnetic wave vectors with spin modulation either along the c axis in $R = \text{Tb, Er and Tm}$, or within the ab plane in $R = \text{Dy and Ho}$.

Keywords: rare earth led binary systems, incommensurate magnetic structure, crystal field effects.

I. INTRODUCTION

The discovery of intermetallic compounds with the chemical formula R_5M_3 ($R = \text{rare earth}$, $M = \text{Si, Ge, Sn, Sb and Bi}$) attracted attention in condensed matter physics because of their rich structural and physical properties. $R_5\text{Si}_3$ compounds ($R = \text{La-Nd}$) crystallize in the Cr_5B_3 -type tetragonal structure^{1, 2} with space group (SG) I_4/mcm , while the $R = \text{Gd-Lu, Y}$, members of this series crystallize in the Mn_5Si_3 -type hexagonal structure with SG $P6_3/mcm$.^{3, 4} All $R_5\text{Bi}_3$ compounds crystallize in the orthorhombic Y_5Bi_3 -type structure with SG $Pnma$.^{2, 5, 6} R_5M_3 (where $R = \text{La-Nd, Gd-Lu}$ and $M = \text{Ge, Sn, Sb, Pb}$) adopt a hexagonal $P6_3/mcm$ structure, in which the R atoms (R_1, R_2) occupy two inequivalent crystallographic sites, with $2(3) R_1(R_2)/\text{f.u.}$ in the $4d(6g)$ positions. Thus one

can expect different magnetic coupling between the two different sublattices leading to the anisotropic exchange and, hence, complex magnetic ordering.

Limited physical properties characterization is reported for the hexagonal R_5M_3 ($M = \text{Si, Ge, Sn}$ and Sb) family of compounds. Yb_5Si_3 is reported to form with mixed-valence Yb ions, showing AFM order below the Néel temperature $T_N = 1.6$ K. Ho_5Si_3 undergoes two magnetic transitions at low temperatures: first, AFM ordering at $T_N = 24$ K, and second, a spin reorientation transition at $T_2 \sim 8$ K. Field-dependent magnetization data reveal a metamagnetic transition at $H_c = 2.2$ T. Later studies by Canepa *et al.*⁷ on $R_5\text{Si}_3$ samples with $R = \text{Y, Ce, Pr, Nd, Sm, Gd, Tb, Yb, and Lu}$ presented temperature-dependent ($T = 4 - 300$ K) resistivity data. However, detailed information on the magnetic properties of the $R_5\text{Si}_3$ is still lacking.

The $R_5\text{Ge}_3$ compounds with $R = \text{Pr, Gd, Tb, Ho, and Er}$ show AFM order with Néel temperatures between $T_N = 10$ and 85 K and ferrimagnetic (FI) order in Nd_5Ge_3 and Ce_5Ge_3 .^{8,9} As expected, La_5Ge_3 and Y_5Ge_3 are Pauli paramagnets. No other magnetic transitions were observed below the ordering temperature in the magnetic $R_5\text{Ge}_3$ series. In 2004, Tsutaoka *et al.*¹⁰ presented the magnetic and transport properties of Gd_5Ge_3 and Tb_5Ge_3 single crystals. Gd_5Ge_3 was found to be AFM below $T_N = 76$ K, with a spin reorientation transition at $T_{SR} \sim 52$ K. Tb_5Ge_3 shows an AFM order below $T_N = 79$ K, with large magnetic anisotropy.¹¹ The antimonides $R_5\text{Sb}_3$ with $R = \text{Pr, Nd, Gd-Tm}$ show AFM order, with Néel temperatures up to 109 K for $R = \text{Gd}$.^{2, 12} Not surprisingly, La_5Sb_3 and Y_5Sb_3 display a temperature-independent susceptibility.²

Magnetization measurements carried out on R_5M_3 ($R = \text{rare earth, } M = \text{Si, Ge, Sn, and Sb}$) compounds revealed the presence of anisotropic exchange interactions or strong crystal field effects (CEF), or both. As a result, these compounds present complex magnetic behavior, mainly due to exchange interaction between two inequivalent R atomic sites. Such a behavior was confirmed by neutron powder diffraction (NPD) in some of the R_5M_3 systems. The magnetic configuration was found to be conical-spiral for Tb_5Sb_3 ,¹³ flat-spiral for Tb_5Ge_3 ,¹⁴ and amplitude sine-modulated for Ho_5Si_3 ,¹ Ho_5Sb_3 ,¹⁵ Dy_5Sb_3 ,¹⁶ Tb_5Sn_3 ,¹⁷ Er_5Sn_3 ,¹⁸ and Ho_5Sn_3 .¹⁹ To better understand the complex interplay between the exchange interactions and CEF in the R_5M_3 compounds, a detailed study on their anisotropic thermodynamic and transport properties is needed.

In this manuscript, we performed such a study of the structural and magnetic properties on the $R_5\text{Pb}_3$ compounds ($R = \text{Gd-Tm}$), from a combination of magnetization and NPD measurements. We investigated the influence of different rare earth metals on the crystal structure and the magnetism.

Lattice parameters and the unit cell volume decrease monotonically with decreasing rare earth ionic radii, according to the expected lanthanide contraction.²⁰ NPD reveals the anisotropy in the $R_5\text{Pb}_3$ systems ($R = \text{Tb-Tm}$) and multiple magnetic transitions in the ordered state, with incommensurate magnetic wave vectors $\mathbf{k}_m$ associated with the ordered state down to the lowest measured temperature ($T = 4$ K). The multiple magnetic transitions observed in NPD are further confirmed by magnetization measurements. Remarkably, after Gd_5Si_4 ($T_{\text{ORD}} = 340$ K),²¹ $R_5\text{Pb}_3$ systems have the highest observed ordering temperatures T_{ORD} compared to other known R - M ($M = \text{Si, Ge, Sn, and Sb}$) binary compounds. For example, Gd_5Pb_3 orders at 275 K, which is much higher than Gd_5Ge_4 ($T_{\text{ORD}} = 127$ K),²² Gd_5Sn_4 ($T_{\text{ORD}} = 80$ K),²³ Gd_5Sn_3 ($T_{\text{ORD}} = 68$ K),¹⁰ Gd_5Si_3 ($T_{\text{ORD}} = 55$ K),⁷ Gd_5Ge_3 ($T_{\text{ORD}} = 52$ K).¹⁰ A striking result of the high anisotropy in the $R_5\text{Pb}_3$ compounds is that the Weiss temperatures θ_W are up to five times smaller than the ordering temperatures T_{ORD} . This was also the case in the high T_{ORD} Gd silicates, for example in GdSi , which has a ordering temperature ($T_{\text{ORD}} = 78$ K) four times larger than the Weiss temperature ($\theta_W = 20$ K).²⁴

II. MATERIALS AND METHODS

Polycrystalline $R_5\text{Pb}_3$ ($R = \text{Gd-Tm}$) samples were prepared from rare earth ingots (Ames lab 99.999%) and Pb (Alfa Aesar; 99.98%) in a molar ratio of 5:3.5, with excess Pb used to compensate for mass losses during heating. Arc melting of the samples was performed on a water-cooled Copper hearth under a purified argon atmosphere. To ensure homogeneity, the samples were turned over and re-melted several times. Initial phase analysis was done using x-ray powder diffraction on a Rigaku D/max ULTIMA II diffractometer with Cu $K\alpha$ radiation source. The $R_5\text{Pb}_3$ ($R = \text{Gd-Tm}$) turned out to be extremely air-sensitive, so the x-ray powders were covered by a layer of amorphous mineral oil. Rietveld analysis²⁵ of the powder diffraction data was done using the GSAS/EXPGUI suite of programs.²⁶ A pseudo-Voigt function was used to describe the peak shape for all data. As an example, the Rietveld fit of the x-ray powder diffraction for Ho_5Pb_3 is shown in Fig. 1. The presence of the mineral oil as a protective layer can be observed as a broad peak at low angles ($2\theta = 10^\circ - 20^\circ$), together with up to 3 wt% of Pb impurity in all polycrystalline $R_5\text{Pb}_3$ samples.

For the NPD experiments, roughly 5 g of each polycrystalline sample was held in a cylindrical vanadium container in a top-loading closed-cycle refrigerator and studied using the HB-2A powder diffractometer at the High Flux Isotope Reactor of Oak Ridge National Laboratory.²⁷ Data from HB-2A were collected with neutron wavelengths $\lambda = 1.54$ Å and $\lambda = 2.41$ Å, by (115) and (113) reflections

from a vertically-focusing Ge monochromator. The data were acquired in the temperature range of 4 – 220 K by scanning the detector array consisting of 44 ^3He tubes in two segments to cover the angle 2θ range of 4° – 150° in steps of 0.05° . Overlapping detectors for the given steps were used to average the counting efficiency of each detector. The shorter wavelength, which gives a greater intensity and higher Q coverage, was used to investigate the crystal structures in this low temperature regime, while the longer wavelength gives lower Q coverage and greater resolution that was important for investigating the magnetic structures of these materials. More details about the HB-2A instrument and data collection strategies can be found in Ref. [27]. The NPD data were analyzed using the Rietveld refinement program FULLPROF²⁸ and the representational analysis software SARAh.²⁹

Powder diffraction patterns reveal that all samples have a hexagonal structure with SG $P6_3/mcm$, in which the rare earth atoms occupy two inequivalent crystallographic $4d$ and $6g$ sites, located at $(1/3, 2/3, 0)$ and $(x_R, 0, 1/4)$. The atoms in the $4d$ position (R_1 in Fig. 2c) are linked into linear chains along the c axis, while the atoms in the $6g$ position (R_2 in Fig. 2c) form face-sharing octahedral chains along c . This structure is similar to that of the R_5M_3 analogues ($M = \text{Si, Ge, Sn}$). Both a (squares, left axis in Fig. 2a) and c (triangles, right axis in Fig. 2a) lattice parameters, as well as the unit cell volume (circles, right axis in Fig. 2b), decrease as expected as R changes from Gd towards Tm in the $R_5\text{Pb}_3$ series. From Rietveld refinements, the distances between the nearest (NN, R_1 - R_1 , R_2 - R_2) and next-nearest (NNN, R_1 - R_2) R neighbors were calculated. The shortest R - R distances $d_{R_1-R_1} = 3.2$ - 3.4 Å were found between R_1 atoms situated in the quasi-one dimensional chains, parallel to the c axis.

Zero field-cooled (ZFC) and field-cooled (FC) DC magnetic susceptibilities were measured using a Quantum Design (QD) Magnetic Property Measurement System (MPMS). The temperature dependence of the susceptibility for all samples was measured in $H = 0.1$ T, with additional fields up to $H = 7$ T measured for a subset of the samples. The AFM transition temperatures T_N and the lower-temperature transitions for the AFM compounds were determined from the peaks in $d(MT)/dT$.³⁰ In the case of FM order, the Curie temperature T_C and all other transition temperatures were determined from susceptibility derivatives dM/dT . To further characterize the magnetic behavior of $R_5\text{Pb}_3$ samples, the field-dependent magnetization measurements $M(H)$ were performed at $T = 2$ K. All $R_5\text{Pb}_3$ samples show metamagnetic phase transitions, with the critical field values determined from the maxima in dM/dH .

III. RESULTS

3.1 Gd₅Pb₃

Fig. 3a shows the ZFC (closed symbols) temperature dependence of the magnetic susceptibility M/H for Gd₅Pb₃ in applied magnetic field $H = 0.1$ T (black circles), 1 T (red triangles) and 7 T (blue squares). The Curie-Weiss law is followed at temperatures above 300 K, as revealed by the linear inverse susceptibility H/M (open circles, right axis, Fig. 3a). The linear fit above ~ 300 K yields a Weiss temperature $\theta_W = 158.7$ K and effective magnetic moment $\mu_{eff}^{exp} \approx 7.46 \mu_B / \text{Gd}^{3+}$, close to the theoretical value $\mu_{eff}^{theory} \approx 7.94 \mu_B$ for Gd^{3+} . The positive θ_W value is indicative of FM coupling, consistent with the shape of the magnetic susceptibility, abruptly increasing below $T_{ORD} \sim 275$ K. More interestingly, θ_W is nearly half of the ordering temperature $T_{ORD} = 275$ K, with T_{ORD} determined from the minimum in dM/dT for $H = 0.1$ T, as shown in Fig. 3b. Below T_{ORD} another magnetic transition is evident at $T_2 = 85.5$ K, as seen in the high field $M(T)$ data (inset, Fig. 3a) and also revealed by the magnetization derivative dM/dT (inset, Fig. 3b).³⁰ The transition temperatures T_{ORD} and T_2 do not change with increasing magnetic field up to $H = 7$ T

Compared to others $R_5\text{Pb}_3$ compounds, the $M(H)$ isotherm for Gd₅Pb₃ (Fig. 4) shows almost linear behavior in the applied magnetic field of $0.2 \text{ T} < H < 7 \text{ T}$. The steep $M(H)$ increase for fields $H < 0.2$ T is reminiscent of the anisotropic behavior in some Gd intermetallic compounds,³¹ suggesting that a helical (or more complex) magnetic moment configuration in Gd₅Pb₃ may be responsible for both the $M(H)$ shape and the small M values reached with $H = 7$ T. No magnetic hysteresis is observed (Fig. 4).

No NPD has been collected on Gd₅Pb₃ due to its very high absorption cross-section for neutrons. For example, Gd₂O₃ is used as a neutron beam stopper.³²

3.2 Tb₅Pb₃

The ZFC (full circles) and FC (full triangles) temperature dependence of the magnetic susceptibility M/H (left axis) and the inverse susceptibility H/M (right axis) is shown in Fig. 5a and reveals two magnetic transitions, first at $T_{ORD} = 215.3$ K and second at $T_2 = 69.4$ K. The values of T_{ORD} and T_2 were determined from peaks in dM/dT . The inverse magnetic susceptibility shows linear temperature dependence above 300 K, indicative of Curie-Weiss behavior. The linear fit H/M above ~ 300 K yields a Weiss temperature $\theta_W = 96.4$ K. This is less than half of T_{ORD} , a likely consequence of strong crystal field effects, or anisotropic coupling, or both. The positive θ_W value indicates the dominance of the FM coupling between the Tb^{3+} magnetic ions. The effective magnetic moment is

$m_{\text{eff}}^{\text{exp}} \approx 9.66 \mu_B/\text{Tb}^{3+}$, which is consistent with the theoretical value calculated for the Tb^{3+} free ion, $\mu_{\text{eff}}^{\text{theory}} \approx 9.72 \mu_B$. The $T = 2$ K $M(H)$ isotherm (black squares, Fig. 5b) shows small hysteresis below $H \sim 2.2$ T. Considering the lack of the secondary phases in the neutron data shown below, the observed small hysteresis in Tb_5Pb_3 measured at $T = 2$ K can be ascribed to a small, intrinsic FM component. The low measured magnetization values $M(H) \leq 2 \mu_B$ at the maximum measured magnetic field $H = 7$ T could be a consequence of the crystal field anisotropy.

The magnetic order in Tb_5Pb_3 is further investigated by the NPD data collected at $T = 300, 150, 90, 70, 60, 50$ K using a wavelength $\lambda = 1.54$ Å, and at $T = 4$ K using $\lambda = 2.41$ Å (Fig. 6). In the paramagnetic state ($T = 300$ K bottom curve in Fig. 6), only the nuclear peaks are visible. As the temperature is decreased through $T = 150$ K, extra intensity on the nuclear (2,1,1) Bragg peak develops at $Q = 2.29$ Å⁻¹ for all lower temperatures. Additional magnetic peaks are observed below $T = 70$ K, in the range $Q = 1 - 2.5$ Å⁻¹, with intensities varying as a function of temperature. Using a larger wavelength $\lambda = 2.41$ Å, a (0,0, l) magnetic peak with $l = 1.52$ is revealed at $T = 4$ K (inset, Fig. 6), suggesting that the spins order along c axis at this temperature.

A careful comparison of the $T = 300$ K and 150 K data (inset, Fig. 7) reveals weak magnetic contributions to the nuclear (1,0,2), (1,1,1), and (2,1,1) Bragg reflections. This is indicative of weak FM coupling of the R spins, which is consistent with the FM ordering observed from magnetization around $T_C = 215.3$ K (Fig. 5a). All magnetic Bragg reflections were indexed with a hexagonal cell $a_M = a_N$, $c_M = c_N$, where the subscript M denotes magnetic and N the nuclear cell. The temperature evolution of the magnetic (2,1,1)+ $\mathbf{k}_m$ Bragg reflection was measured in the temperature range $T = 150$ K - 260 K, and its intensity is shown in Fig. 7 (black squares). The intensity of this peak increases in the ordered state, resulting in an estimate of the ordering temperature $T_{\text{ORD}} = 211$ K, taken as the intercept of the two solid lines in Fig. 7. This is in good agreement with the magnetization data shown in Fig. 5a.

Upon further cooling, the new magnetic peaks developing below $T = 70$ K point to an AFM state in this temperature range. Indexing these magnetic peaks suggests that the magnetic unit cell is almost twice as large as the nuclear unit cell with $a_M = a_N$ and $c_M = 1.88c_N$. The corresponding propagation magnetic vector below $T = 60$ K is $\mathbf{k}_{m1} = (0,0,0.535)$, as shown in Fig. 8a. At 4 K, the incommensurability changes, with the corresponding magnetic vector $\mathbf{k}_{m2} = (0,0,0.520)$ seen in Fig. 8b. A detailed analysis of the magnetic structure in Tb_5Pb_3 is underway, to be published elsewhere.³³ The peak at $Q = 2.29$ Å⁻¹ persists throughout the AFM state (Fig. 8), making it unclear whether it is intrinsic

to the AFM order or if it is associated with a FM component within the AFM state.

3.3 Dy₅Pb₃

Fig. 9a shows the ZFC (circles) and FC (triangles) temperature-dependent magnetic susceptibility M/H (left axis) and the inverse susceptibility H/M (open symbols, right axis), measured in an applied field $H = 0.1$ T. By contrast with the $R = \text{Gd}$ and Tb compounds, where $M(T)$ diverged at T_{ORD} (Figs. 3a and 5a), in Dy_5Pb_3 the magnetic order is indicated by a peak close to 160 K. The shape of the magnetic susceptibility and the indistinguishable ZFC/FC $M(T)$ close to this temperature suggest that the transition corresponds to AFM order, with the Néel temperature T_N determined from $d(MT)/dT^{23}$ to be $T_N = 160.6$ K. However, the upturn in the magnetization and the additional peaks at lower temperatures reveal very complex magnetic behavior in Dy_5Pb_3 . Three local magnetization maxima at $T_2 = 75.3$ K, $T_3 = 43.3$ K and $T_4 = 15.4$ K are determined from the $d(MT)/dT$, with small ZFC/FC irreversibility observed below T_2 . The spin reorientation transitions at T_2 - T_4 might also be associated with a small FM component at low temperatures. The inverse magnetic susceptibility displayed in Fig. 9a (right axis) is linear above 220 K, indicative of Curie-Weiss behavior. From the linear fit of H/M above $T = 220$ K, the resulting Weiss temperature is $\theta_W = 36.4$ K, with the effective moment $m_{\text{eff}}^{\text{exp}} \approx 10.38 \mu_B/\text{Dy}^{3+}$, consistent with the theoretical value $\mu_{\text{eff}}^{\text{theory}} \approx 10.63 \mu_B/\text{Dy}^{3+}$. The positive θ_W value indicates FM coupling between Dy^{3+} ions. It is very likely then that a combination of strong CEF effects and anisotropic exchange interactions result in the AFM order, and are responsible for the remarkably large ordering temperature (almost five times) compared to θ_W .

The $M(H)$ isotherm measured at $T = 2$ K (Fig. 9b) displays one broad metamagnetic transition at $H_c = 5.9$ (6.25) T for increasing (decreasing) applied field, as determined from the peaks position in the dM/dH plot (inset, Fig. 9b). The magnetization in the maximum applied field $H = 7$ T ($\sim 5.8 \mu_B / \text{Dy}^{3+}$) is close to half of the Dy^{3+} saturated moment $\mu_{\text{sat}} = 10 \mu_B/\text{Dy}^{3+}$. It is therefore likely that more metamagnetic transitions may occur in higher magnetic fields. Small hysteresis can be observed for the whole measured field range, a likely result of the FM component at low temperatures, as suggested by the ZFC/FC irreversibility in $M(T)$ data (Fig. 9a).

Neutron diffraction measurements on Dy-containing samples are inherently difficult given that Dy is a strong neutron absorber. However, measurements on Dy_5Pb_3 did reveal two magnetic peaks between $T = 30$ K and 4 K, marked by the vertical arrows in Fig. 10a. These magnetic peaks were identified by comparison with the measurement in the paramagnetic state $T = 250$ K (bottom curve,

Fig. 10a). The order parameter for Dy_5Pb_3 , measured on the $(-3,1,1)+\mathbf{k}_m$ magnetic Bragg reflection in the temperature range $T = 4 - 95$ K (Fig. 10b) reveals the third magnetic transition at $T_3 = 39$ K. This is close to the value determined from magnetization $T_3 = 43.3$ K (Fig. 9a). The magnetic peaks are consistent with a magnetic wavevector $\mathbf{k}_m = (0,0.301,0)$, determined from the Le Bail fit of the $T = 4$ K NPD data (Fig. 11).

3.4 Ho_5Pb_3

Fig. 12a shows the temperature-dependent magnetic susceptibility M/H (black circles, left axis) and the inverse susceptibility H/M (open circles, right axis) for Ho_5Pb_3 in an applied field $H = 0.1$ T. No ZFC/FC irreversibility was registered down to 1.8 K, which, together with the weak peak around 110 K, suggest AFM order in this compound. The Néel temperature T_N was determined from $d(MT)/dT$ to be $T_N = 111$ K. Upon further cooling, two local magnetization maxima at $T_2 = 23.7$ K and $T_3 = 8.03$ K are determined from the $d(MT)/dT$. The inverse magnetic susceptibility displayed in Fig. 12 (right axis) is linear above 110 K, indicative of Curie-Weiss behavior. From the linear fit of H/M above $T = 110$ K, the resulting Weiss temperature is $\theta_W = 30.4$ K, with the effective moment $m_{\text{eff}}^{\text{exp}} \approx 10.95 \mu_B/\text{Ho}^{3+}$ close to the theoretical value $\mu_{\text{eff}}^{\text{theory}} \approx 10.61 \mu_B/\text{Ho}^{3+}$. The positive θ_W value indicates FM coupling between Ho^{3+} ions. However, the evidence for magnetic order from $M(T)$ data points to AFM order, suggesting possible anisotropic spin coupling and strong CEF effects, as well as the remarkably large ordering temperature T_{ORD} compared to θ_W , $T_{\text{ORD}}/\theta_W \sim 4$.

The $T = 2$ K $M(H)$ isotherm (Fig. 12b) shows two metamagnetic transitions up to $H = 7$ T, also consistent with spin-flop transitions in the AFM state. However, within our field range the maximum magnetization ($\sim 3 \mu_B/\text{Ho}^{3+}$) is less than half the Ho^{3+} saturated moment $\mu_{\text{sat}}(\text{Ho}^{3+}) = 10.6 \mu_B$. It is therefore likely that more metamagnetic transitions occur in higher magnetic fields.

Fig. 13 shows the temperature evolution of the $(3,-1,0)+\mathbf{k}_{m1}$, $(1,0,0)+\mathbf{k}_{m2}$, and $(0,1,0)+\mathbf{k}_{m2}+\mathbf{k}_{m3}$ peaks as the most intense Ho_5Pb_3 magnetic Bragg peaks for the respective temperature intervals. The order parameter for Ho_5Pb_3 measured on the $(3,-1,0)+\mathbf{k}_{m1}$ magnetic Bragg reflection in the temperature range $T = 70 - 120$ K reveals the ordering temperature $T = 110.5$ K, taken as the intercept of the two solid lines in Fig. 13a. This is close to the value determined from magnetization $T_{\text{ORD}} = 111$ K. The $(1,0,0)+\mathbf{k}_{m2}$ and $(0,1,0)+\mathbf{k}_{m2}+\mathbf{k}_{m3}$ magnetic Bragg reflections measured in the temperature range $T = 4 - 40$ K (Fig. 13b) were used to determine the magnetic transition temperatures $T_2 \sim 28.6$ K and $T_3 \sim 8.7$ K. These transition temperatures are close to the values determined from the magnetic susceptibility

in Fig. 12a.

Fig. 14 shows the NPD data for Ho_5Pb_3 measured at $T = 50$ K. Indexing the magnetic peaks suggests that the magnetic unit cell is more than three times larger than the nuclear unit cell with $a_M = 3.46a_N$ and $c_M = c_N$. The corresponding propagation magnetic vector determined from the Le Bail fit of the $T = 50$ K NPD data (Fig. 14) is $\mathbf{k}_{m1} = (0, 0.295, 0)$. The $(h, k, 0)$ magnetic peak with $h = 1$ and $k = 0.295$ at $T = 50$ K (left inset, Fig. 14) suggests that the Ho spins order within the ab plane at this temperature. The right inset (Fig. 14) shows a comparison of the NPD patterns for Ho_5Pb_3 collected at temperatures $T = 150$ K (purple) and 300 K (black) plotted in $Q = 1.75\text{--}2.3 \text{ \AA}^{-1}$ interval.

With the second magnetic transition at $T_2 = 28.6$ K, the incommensurability of the magnetic vector changes to $\mathbf{k}_{m2} = (0, 0.288, 0)$ (orange, Fig. 15a). Below $T_3 = 8.7$ K, the additional AFM ordering along the b axis is indexed using $\mathbf{k}_{m3} = (0, 0.5, 0)$ (blue, Fig. 15b). At $T = 4$ K, all magnetic Bragg reflections are indexed using the same two magnetic propagation vectors $\mathbf{k}_{m2}$ and $\mathbf{k}_{m3}$, with an additional rotation of the spins towards the basal plane.

3.5 Er_5Pb_3 .

Fig. 16a shows the temperature-dependent magnetic susceptibility M/H (full symbols, left axis) and the inverse susceptibility H/M (open symbols, right axis) for Er_5Pb_3 in an applied field $H = 0.1$ T. The magnetic order is marked by a peak in M/H close to 36 K and, together with the indistinguishable ZFC/FC $M(T)$ close to this temperature, suggests that the transition corresponds to AFM order. The Néel temperature T_N determined from $d(MT)/dT$ is $T_N = 36.3$ K. Upon further cooling, another local magnetization maximum at $T_2 = 11.0$ K is observed in $d(MT)/dT$, consistent with a spin reorientation transition. The inverse magnetic susceptibility displayed in Fig. 16 (right axis) is linear above 50 K, indicative of Curie-Weiss behavior. From the linear fit of H/M above $T = 50$ K, the resulting Weiss temperature is $\theta_W = 21.3$ K, with the effective moment $m_{eff}^{exp} \approx 9.62 \mu_B/\text{Er}^{3+}$. This is consistent with the calculated value $\mu_{eff}^{theory} \approx 9.58 \mu_B/\text{Er}^{3+}$. As was also the case for $R = \text{Dy}$ and Ho , the positive θ_W value indicates FM coupling between Er^{3+} ions, which, together with likely strong CEF effects, results in the AFM order. As was the case for the other R members of this series, the ordering temperature T_N exceeds the Weiss temperature, and in this case $T_N/\theta_W \sim 2$.

The $T = 2$ K $M(H)$ isotherm (Fig. 16b) displays a metamagnetic transition with the critical field $H_c = 1.25$ (2.37) T for increasing (decreasing) applied field, as determined from the peak position in dM/dH . The metamagnetism is likely associated with spin-flop transitions caused by strong CEF

anisotropy in this system. It was shown³⁴ that in antiferromagnets with strong uniaxial anisotropy, *e.g.* hexagonal or tetragonal systems with an easy axis, the transition would be a single-step from a low magnetization state toward a fully saturated state. However, within our field range the maximum magnetization ($\sim 8 \mu_B/\text{Er}^{3+}$) is less than the Er^{3+} saturated moment $\mu_{\text{sat}} = 9 \mu_B/\text{Er}^{3+}$. The finite slope of $M(H)$ at $H = 7$ T suggests that this system is approaching saturation at a field slightly higher than our maximum measured field.

Fig. 17 shows a comparison of the NPD patterns for Er_5Pb_3 collected at $T = 150, 60, 20$ and 4 K, using wavelength $\lambda = 1.54 \text{ \AA}$ and plotted in the $Q = 0.4 - 2.6 \text{ \AA}^{-1}$ interval. Fig. 18 shows the LeBail refinement of the NPD data for Er_5Pb_3 measured at $T = 20$ K (a) and 4 K (b). The insets show NPD data for $Q = 0.1-1.3 \text{ \AA}^{-1}$. Below $T = 20$ K the NPD data (Fig. 18a) reveals new magnetic Bragg reflections compared to the high temperature data ($T = 150$ K, Fig. 17) indicative of AFM state. This is in good agreement with the magnetization data with AFM ordering below $T_N = 36.3$ K. Indexing the new magnetic peaks suggests that the magnetic unit cell is more than three times larger than the nuclear unit cell with $a_M = a_N$, $c_M = 3.40c_N$. The corresponding propagation magnetic vector determined from the LeBail fit to the $T = 20$ K NPD data (Fig. 18a) is $\mathbf{k}_{\text{m1}} = (0,0,0.294)$. A second magnetic transition observed in the magnetization data at $T_2 = 11$ K is caused by an additional spin rotation along the c axis (Fig. 18b). At $T = 4$ K, intensities of the $(h,h,0)+\mathbf{k}_m$ magnetic peaks decrease compared to those measured at $T = 20$ K, typical of a spin rotation from an in-plane to an out-of-plane arrangement. In our case, out-of-plane spin arrangements lower the magnetic component along the c axis, leading to an intensity decrease of the $(h,h,0)+\mathbf{k}_m$ magnetic peaks.

3.6 Tm_5Pb_3 .

Fig. 19a shows the temperature-dependent magnetic susceptibility M/H (black circles, left axis) and the inverse susceptibility H/M (open circles, right axis) for Tm_5Pb_3 in an applied field of $H = 0.1$ T. The magnetic order is marked by a peak in M/H close to 18 K and, together with the indistinguishable ZFC/FC $M(T)$ close to this temperature, suggests that the transition corresponds to AFM order. The Néel temperature T_N determined from $d(MT)/dT$ is $T_N = 17.8$ K. The inverse magnetic susceptibility displayed in Fig. 19a (right axis) is linear above 16 K, indicative of Curie-Weiss behavior. From the linear fit of H/M above $T = 40$ K, the resulting Weiss temperature is $\theta_W = -1.7$ K, with the effective moment $m_{\text{eff}}^{\text{exp}} \approx 7.45 \mu_B/\text{Tm}^{3+}$. This is consistent with the calculated value $\mu_{\text{eff}}^{\text{theory}} \approx 7.56 \mu_B/\text{Tm}^{3+}$. The negative θ_W value confirms the AFM coupling between Tm^{3+} ions.

The $M(H)$ isotherm measured at $T = 2$ K (Fig. 19b) displays metamagnetic transitions with a critical field for increasing (decreasing) applied field, as determined from the peaks in the dM/dH . The magnetization in an applied field $H = 7$ T corresponds to $7 \mu_B/\text{Tm}^{3+}$ and is consistent with the calculated saturated moment $\mu_{sat} = 7 \mu_B/\text{Tm}^{3+}$.

NPD patterns for Tm_5Pb_3 collected at $T = 150, 50, 30$ and 4 K using a wavelength $\lambda = 1.54 \text{ \AA}$ are shown in Fig. 20, for $Q = 0.70 - 2.8 \text{ \AA}^{-1}$. Magnetic peaks are revealed at $T = 4$ K compared to the higher temperature measurements, suggesting AFM magnetic order between 30 and 4 K. Indexing these magnetic peaks suggests that the magnetic unit cell is more than three times larger than the nuclear unit cell with $a_M = a_N$, $c_M = 3.60c_N$. The corresponding propagation magnetic vector determined from the Le Bail fit to the $T = 4$ K NPD data (Fig. 20) is $\mathbf{k}_{\text{ml}} = (0,0,0.275)$. Such a magnetic vector is similar to the one found in Er_5Pb_3 or Er_5Si_3 .²⁴

IV. CONCLUSIONS

We have successfully synthesized polycrystalline $R_5\text{Pb}_3$ ($R = \text{Gd-Tm}$) samples and performed structural and magnetic analysis, along with NPD for the $R_5\text{Pb}_3$ ($R = \text{Gd-Tm}$) compounds. The inverse magnetic susceptibilities of all $R_5\text{Pb}_3$ showed that the ordering temperature T_{ORD} (either T_N or T_C) decreases when going from Gd^{3+} towards Tm^{3+} (Fig. 21a), consistent with the expected deGennes scaling.³⁵ Below T_{ORD} , the behavior is complex and reveals additional phase transitions at T_2, T_3, T_4 . A fit of the linear parts of the H/M to the Curie-Weiss law yields large differences between Weiss temperatures θ_W and the actual T_{ORD} (Fig. 21), with the latter several times larger than the former temperature. In the absence of strong CEF anisotropy or other competing energy scales, T_{ORD} and $|\theta_W|$ are expected to be very similar. Big differences between the two temperatures often result because of frustration,³⁶ with θ_W about one or two orders of magnitude larger than T_{ORD} . However, in the $R_5\text{Pb}_3$ compounds reported here (for $R = \text{Gd} - \text{Tm}$), T_{ORD} is actually several times larger than θ_W , a remarkable and rare occurrence in magnetic materials. This is clearly not due to frustration, but likely the result of strong CEF effects, or large anisotropic exchange between the two R sublattices, which is consistent with other observations regarding the coupling inferred from θ_W and the observed ordering. Although the Curie-Weiss fits yield positive θ_W values for $R_5\text{Pb}_3$ ($R = \text{Gd} - \text{Er}$), NPD analysis indicates more complex ordered states. This is possibly caused by the competing exchange interactions between the two inequivalent R atomic sites, and is often accompanied by the competition between magnetic incommensurability and commensurability.¹³⁻¹⁹

The $T = 2$ K isotherms for $R_5\text{Pb}_3$ with $R = \text{Tb} - \text{Tm}$ compounds reveals metamagnetic behavior associated with the crystal field anisotropy. For $R_5\text{Pb}_3$ ($R = \text{Tb}$ and Dy), the S -shaped isotherms and their smooth variation in the measured field range is typical of a continuous metamagnetic transition, which is generally of second order. Note that hysteresis is almost nonexistent in $R_5\text{Pb}_3$ ($R = \text{Tb}$ and Dy) isotherms. The opposite was observed for Er_5Pb_3 . The isotherm for Er_5Pb_3 shows a step-like metamagnetic transition with pronounced hysteresis. Such discontinuous behavior is usually, but not always, associated with a first-order transition. The same isotherms for $R_5\text{Pb}_3$ with $R = \text{Ho}$ and Tm show multiple metamagnetic transitions. Due to the polycrystallinity and air-sensitivity of our samples, one cannot fully describe the inter-ionic interactions between R sites. It is evident that the CEF effects, anisotropic or competing exchange interactions, frustration (hexagonal structure with two inequivalent crystallographic R sites), and magnetic coupling play a leading role in the complex magnetic properties observed in $R_5\text{Pb}_3$. However single crystals will be necessary to pinpoint the exact magnetic spin configurations in these compounds, and this is the subject of an ongoing study.

The ordering temperatures T_{ORD} follow the expected de Gennes scaling $T_{\text{ORD}} \sim \text{dG}$, where the deGennes factor dG is given by $\text{dG} = (g_J - 1)^2 J(J + 1)$, in which g_J is the Landé factor and J is the total angular momentum of the R^{3+} ion Hund's rule ground state multiplet. The magnetic ordering temperatures (T_{ORD} , T_2 , T_3 , T_4), Weiss temperatures θ_W and the ratio $f = |\theta_W| / T_{\text{ORD}}$ for $R_5\text{Pb}_3$ ($R = \text{Gd} - \text{Tm}$) are shown in Fig. 21. The dashed line in Fig 21a shows the expected linear de Gennes scaling. CEF effects often reduce the Hund's rule ground state degeneracy, leading to deviations from the Curie-Weiss behavior of the temperature-dependent magnetic susceptibility. In our case, such a behavior manifests itself in T_{ORD} being much higher than the Weiss temperature θ_W . The ratio, $f = |\theta_W| / T_{\text{ORD}}$, or the frustration parameter, is usually employed to quantify the frustration in magnetic systems. With frustration, f is close to 10, or at least larger than unity. This ratio in $R_5\text{Pb}_3$ ($R = \text{Gd} - \text{Tm}$) is notably up to an order of magnitude *smaller* than one, which implies strong crystalline anisotropy or anisotropic exchange between the two R sublattices in these materials.

Like most of the previously studied R_5X_3 compounds ($X = \text{Si}$, Ge , Sn , Sb), complex magnetic structures are also detected in $R_5\text{Pb}_3$ ($R = \text{Gd} - \text{Tm}$). For the Pb compounds, NPD data reveal the presence of multiple magnetic phases, which appear to be incommensurate for all $R_5\text{Pb}_3$. As quoted above, in a large number of the magnetic materials the periodicity near T_N is incommensurate or long period-commensurate leading to amplitude-modulated magnetic structures. Only a few known compounds exhibit simple commensurate AFM structures over the whole temperature range below T_N

(e.g. ErGa_2).³⁷ The analysis of our NPD data shows that magnetic propagation vectors $\mathbf{k}_m$ for $R_5\text{Pb}_3$ changes with R as follows: Tb (1, 1, 1.88), Dy (1, 3.333, 1), Ho (1, 3.46, 1), Er (1, 1, 3.40) and Tm (1, 1, 3.63), indicating that the $R = \text{Dy}$ and Ho compounds have magnetic spins aligned in the ab plane, while in the $R = \text{Tb}$, Er , Tm magnetic spins are aligned along the c axis. At $T = 4$ K, a spin rotation occurs in the $R = \text{Tb}$, Ho and Er members of this series, which was observed in other rare earth intermetallics.³⁴ In these systems, except in the case of a non-magnetic CEF singlet ground state, amplitude modulated magnetic structures are proved not to be stable at low temperature, and additional spin rotation or reorientation is observed.³⁴

Based on the increasing c/a ratio (Table 2), it is obvious that the a axis decreases more compared to the c axis with heavier R ions. In other words, upon decreasing the R ionic size, the in-plane d_{R2-R2} distance decreases more than the out-of-plane d_{R2-R2} distance. This possibly decreases the frustration and allows magnetic spins to order within the ab plane in some $R_5\text{Pb}_3$. Thus, by geometry, increasing in-plane anisotropy should be expected going from Tb towards Tm. But, as can be seen from neutron data (Table 1), only Dy_5Pb_3 and Ho_5Pb_3 show in-plane magnetic ordering. In the other $R_5\text{Pb}_3$ ($R = \text{Tb}$, Er and Tm) the magnetic spins are aligned along the c axis. Neutron data and the magnetic $\mathbf{k}$ vectors reveal that CEF effects play a very important role in dictating the magnetic order and spin configuration. For the smaller members of the series, $R = \text{Er}$ and Tm , correlations along the c axis are much stronger than, for example, in the $R = \text{Tb}$ compound, which is why the former compounds have larger correlation lengths (more than 3 unit cells along the c axis).

As one can see from Tables 1 and 2, there is no obvious trend that could explain the complex magnetic behavior observed in $R_5\text{Pb}_3$; rather the c/a ratio, the temperature ratio f and the $\mathbf{k}$ vectors have to be considered together to describe the competition of the in-plane and out-of-plane d_{R2-R2} magnetic interactions. The character of the modulations and detailed analysis of the NPD data together with the representational symmetry analysis will be published separately.³³ Inelastic neutron scattering and single crystals of the $R_5\text{Pb}_3$ are needed in order to determine the crystal field parameters, which would describe quantitatively the complex magnetic behavior observed in $R_5\text{Pb}_3$ compounds.

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Table 1: Measured and calculated magnetic moment, ordering temperatures, Weiss temperature, and incommensurate magnetic structures for $R_5\text{Pb}_3$ series.

$R_5\text{Pb}_3$	$\mu_{\text{eff}} (\mu_B/\text{R}^{3+})$		$T_{\text{ORD}} (\text{K})$	$\theta_W (\text{K})$	Magnetic structure
	experimental	theoretical			
Gd₅Pb₃	7.46	7.94	$T_C = 275$ $T_2 = 85.5$ $T_3 = 4.9$	158.7	No NPD data
Tb₅Pb₃	9.66	9.72	$T_C = 215.3$ $T_2 = 69.4$ $T_3 = 4$	115	$\mathbf{k}_{\text{m1}} = (0, 0, 0.535)$ $\mathbf{k}_{\text{m2}} = (0, 0, 0.520)$
Dy₅Pb₃	10.38	10.63	$T_N = 160.6$ $T_2 = 75.3$ $T_3 = 43.3$ $T_4 = 15.4$	36.4	-* -* -* $\mathbf{k}_{\text{m}} = (0, 0.301, 0)$
Ho₅Pb₃	10.61	10.95	$T_N = 111$ $T_2 = 23.7$ $T_3 = 8.0$ $T_4 = 4$	30.4	$\mathbf{k}_{\text{m1}} = (0, 0.295, 0)$ $\mathbf{k}_{\text{m2}} = (0, 0.288, 0)$ $\mathbf{k}_{\text{m2}} + \mathbf{k}_{\text{m3}} = (0, 0.5, 0)$ $\mathbf{k}_{\text{m2}} + \mathbf{k}_{\text{m3}} + \text{spin rotation}$ towards <i>ab</i> plane
Er₅Pb₃	9.62	9.58	$T_N = 36.6$ $T_2 = 11$	21.3	$\mathbf{k}_{\text{m1}} = (0, 0, 0.294)$ $\mathbf{k}_{\text{m1}} + \text{spin rotation}$ towards along <i>c</i> axis
Tm₅Pb₃	7.45	7.56	$T_N = 17.8$	-1.7	$\mathbf{k}_{\text{m1}} = (0, 0, 0.275)$

* No magnetic peaks were observed above $T = 30$ K due to the high neutron absorbance of Dy (see text).

Table 2: Room temperature lattice constants, c/a ratio, and all R - R bond distances for $R_5\text{Pb}_3$ series.

$R_5\text{Pb}_3$	Gd	Tb	Dy	Ho	Er	Tm
a (Å)	9.0879(4)	9.0104(7)	8.9612(5)	8.9100(6)	8.8724(2)	8.8286(3)
c (Å)	6.6487(5)	6.5943(5)	6.5641(4)	6.5326(5)	6.5148(2)	6.49017(2)
c/a	0.7316(4)	0.7319(6)	0.7325(4)	0.7332(5)	0.7343(2)	0.7351(2)
$d_{\text{R1-R1}}$ (Å) ⁺	3.3182(4)	3.2962(3)	3.2813(3)	3.2628(2)	3.2474(3)	3.2329(4)
$d_{\text{R1-R2}}$ (Å)	3.8998(4)	3.9058(2)	3.8583(2)	3.8390(2)	3.8338(2)	3.7977(5)
$d_{\text{R2-R2}}$ (Å) out-of-plane *	3.9729(4)	3.9066(2)	3.8831(2)	3.8831(2)	3.8544(2)	3.8565(3)
$d_{\text{R2-R2}}$ (Å) in-plane *	3.7844(4)	3.6319(3)	3.6880(3)	3.6469(2)	3.5963(3)	3.6417(3)

⁺ $d_{\text{R1-R1}}$ bonds are depicted in Fig. 2c

* $d_{\text{R2-R2}}$ out-of-plane (dash light blue line) and $d_{\text{R2-R2}}$ in-plane (solid light blue line) bonds are depicted in Fig. 2d

FIGURE CAPTIONS

Fig. 1: Rietveld analysis of powder XRD of Ho_5Pb_3 , with collected data (black crosses) and calculated model (red line). The blue vertical lines correspond to calculated Bragg peak positions of the Ho_5Pb_3 phase, while black asterisks mark the Pb impurity.

Fig. 2: (a) The lattice parameters a (left axis) and c (right axis) versus $r_{R^{3+}}$ for $R_5\text{Pb}_3$. (b) The c/a ratio (left axis) along with the volume (right axis) as a function of $r_{R^{3+}}$. The crystal structure of $R_5\text{Pb}_3$ with (c) linear chains of R_1 atoms along the c axis (pink solid arrow corresponds to the $d_{R_1-R_1}$ bond distance); and (d) distorted R_2 hexagonal rings and R_1 honeycomb layers (dark blue line). Also depicted are the in-plane $d_{R_2-R_2}$ (solid light blue line) and out-of-plane $d_{R_2-R_2}$ (dash light blue line) bond distances.

Fig. 3: (a) Temperature-dependent magnetic susceptibility of Gd_5Pb_3 (left axis), measured in different magnetic fields $H = 0.1$ T, 1 T, and 7 T. The inverse magnetic susceptibility (open circles, right axis) along with a Curie-Weiss fit (solid line, right axis). The inset shows a magnetic transition observed at low temperatures. (b) dM/dT for Gd_5Pb_3 for $H = 0.1$ T (left axis). Inset displays the $d(MT)/dT$ for Gd_5Pb_3 for $H = 1$ T.

Fig. 4: The field-dependent magnetization $M(H)$ at $T = 2$ K for Gd_5Pb_3 . The inset corresponds to the low magnetic field region.

Fig. 5: (a) ZFC and FC temperature dependence of the magnetic susceptibility (left axis) and inverse magnetic susceptibility of Tb_5Pb_3 (right axis) measured in $H = 0.1$ T. The solid red line is a Curie-Weiss fit. (b) The magnetic isotherm $M(H)$ measured at $T = 2$ K. The inset shows a hysteresis observed at low magnetic fields ($H < 2.2$ T).

Fig. 6: Comparison of the NPD patterns for Tb_5Pb_3 , collected at various temperatures, using wavelength of $\lambda = 1.54$ Å. The inset shows the NPD data measured at $T = 2$ K using wavelength $\lambda = 2.41$ Å in the range of $Q = 0.2 - 1.8$ Å⁻¹ revealing the most intense $(0, 0, 1) + \mathbf{k}_{m2}$ magnetic peak at $Q \sim 0.5$ Å⁻¹.

Fig. 7: (a) The temperature evolution of the $(2, 1, 1) + \mathbf{k}_m$ magnetic Bragg reflection, as the most intense magnetic peak below the ordering temperature T_{ORD} of Tb_5Pb_3 . An inset depicts the FM contribution on top of the nuclear peaks (black arrows) by overlaying data collected at $T = 300$ K (black line) and $T = 150$ K (red line).

Fig. 8: LeBail refinement of the NPD data for Tb_5Pb_3 measured at $T =$ (a) 60 K and (b) 4 K. The

difference between the measured data (black) and the LeBail fit (red) is shown as a blue line, the calculated Bragg positions are indicated by vertical markers (upper - nuclear phase, lower - magnetic phase). The insets show the difference in incommensurability of the magnetic structures with a magnetic propagation vectors (a) $\mathbf{k}_{m1} = (0, 0, 0.535)$ at $T = 60$ K and (b) $\mathbf{k}_{m2} = (0, 0, 0.520)$ at $T = 4$ K.

Fig. 9: (a) ZFC and FC temperature-dependence of the magnetic susceptibility (left axis) and (b) inverse magnetic susceptibility (right axis) for Dy_5Pb_3 for $H = 0.1$ T. The solid red line is a Curie-Weiss fit. (b) The magnetization isotherm $M(H)$ at $T = 2$ K. The inset shows dM/dH , with a vertical arrow indicating the metamagnetic transition.

Fig. 10: (a) Comparison between the NPD patterns collected at different temperatures for Dy_5Pb_3 . Black arrows indicate magnetic Bragg peaks. The inset shows the temperature evolution of the two magnetic Bragg peaks marked by black arrows. (b) The temperature evolution of the $(-3,1,1)+\mathbf{k}_m$ Bragg reflection, as the most intense magnetic Bragg peak. The solid black line is a guide to the eye.

Fig. 11: LeBail refinement of the NPD data for Dy_5Pb_3 measured at $T = 4$ K. The difference between the measured data (black) and LeBail fit (red) is shown as a blue line, the calculated Bragg positions are indicated by vertical markers (upper - nuclear phase, lower - magnetic phase). The inset shows the LeBail fit in the $Q = 0.9 - 3.0 \text{ \AA}^{-1}$ interval.

Fig. 12: (a) ZFC Ho_5Pb_3 temperature-dependent magnetic susceptibility (left axis) and inverse magnetic susceptibility (right axis) for $H = 0.1$ T. The solid red line is a Curie-Weiss fit. (b) The magnetic isotherm $M(H)$ measured at $T = 2$ K.

Fig. 13: (a) The temperature evolution of the Ho_5Pb_3 $(3,-1,0)+\mathbf{k}_{m1}$ Bragg reflection, as a most intense magnetic Bragg peak below the ordering temperature T_{ORD} . (b) The temperature evolution of the $(1,0,0)+\mathbf{k}_{m2}$ Bragg reflection revealing the second magnetic transition at T_2 . An inset shows the temperature evolution of the $(0,1,0)+\mathbf{k}_{m2}+\mathbf{k}_{m3}$ magnetic Bragg reflection indicating the third magnetic transition at T_3 .

Fig. 14: LeBail refinement of the NPD data for Ho_5Pb_3 measured at $T = 50$ K using magnetic propagation vector $\mathbf{k}_m = (0,0.295,0)$. The difference between the measured data (black) and LeBail fit (red) is shown as a blue line, with the calculated Bragg positions indicated by vertical markers (upper - nuclear phase, lower - magnetic phase). The left inset shows a NPD data for Ho_5Pb_3 plotted in an interval $Q = 0.15 - 0.6 \text{ \AA}^{-1}$. The right inset shows a comparison of the NPD patterns for Ho_5Pb_3

collected at temperatures $T = 150$ K (purple) and 300 K (black) plotted in $Q = 1.75$ - $2.3 \text{ \AA}^{-1}$ interval.

Fig. 15: NPD data for Ho_5Pb_3 at (a) $T = 50$ K (brown), 15 K (orange) and (b) $T = 15$ K (orange), 4 K (blue). The magnetic phase at $T = 15$ K (orange) corresponds to a magnetic propagation vector $\mathbf{k}_{m2} = (0, 0.288, 0)$ and the additional magnetic phase at $T = 4$ K corresponds to a magnetic propagation vector $\mathbf{k}_{m2} + \mathbf{k}_{m3} = (0, 0.5, 0)$.

Fig. 16: (a) ZFC and FC Er_5Pb_3 temperature-dependent magnetic susceptibility (left axis) and inverse magnetic susceptibility H/M (right axis) for $H = 0.1$ T (left axis). The solid red line is a Curie-Weiss fit. The inset shows an irreversibility between ZFC and FC data plotted in the temperature interval $T = 2 - 45$ K. (b) Magnetic isotherm $M(H)$ measured at $T = 2$ K.

Fig. 17: Comparison of the NPD patterns collected at various temperatures for Er_5Pb_3 .

Fig. 18: LeBail refinement of the NPD data for Er_5Pb_3 measured at $T =$ (a) 20 K and (b) 4 K using magnetic propagation vector $\mathbf{k}_m = (0, 0, 0.294)$. The difference between the measured data (black) and LeBail fit (red) is shown as a blue line, with the calculated Bragg positions indicated by vertical markers (upper - nuclear phase, lower - magnetic phase). The insets show NPD data for Er_5Pb_3 plotted in an interval $Q = 0.1 - 1.3 \text{ \AA}^{-1}$ at (a) $T = 20$ K and (b) $T = 4$ K. Arrows highlight the intensity difference of the $(h, h, 0)$ magnetic peaks in the $Q = 0.1$ - $0.9 \text{ \AA}^{-1}$ interval.

Fig. 19: (a) ZFC temperature-dependent magnetic susceptibility (left axis) and inverse magnetic susceptibility H/M (right axis) for Tm_5Pb_3 for $H = 0.1$ T. The solid red line is a Curie-Weiss fit. The inset shows low temperature ZFC magnetic susceptibility for Tm_5Pb_3 . (b) The magnetization isotherm $M(H)$ measured at $T = 2$ K.

Fig. 20: LeBail refinement of the NPD data for Tm_5Pb_3 measured at $T = 4$ K using magnetic propagation vector $\mathbf{k}_m = (0, 0, 0.275)$. The difference between the measured data (black) and LeBail fit (red) is shown as a blue line, with the calculated Bragg positions indicated by vertical markers (upper - nuclear phase, lower - magnetic phase). The inset shows the comparison of the NPD patterns collected at different temperatures for Er_5Pb_3 plotted in the $Q = 0.7 - 2.6 \text{ \AA}^{-1}$ interval.

Fig. 21: (a) Magnetic ordering temperatures (left axis) and Weiss temperature θ_w (right axis) as a function of R ($R = \text{Tm} - \text{Gd}$). The dashed line shows the expected de Gennes scaling. (b) Frustration parameter $f = |\theta_w| / T_{ORD}$ as a function of R .

Fig. 1.

Fig. 2.

FIG. 3.

Fig.4

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FIG. 15

FIG. 16

FIG. 17

FIG. 18

FIG. 19

FIG. 20

FIG. 21