Er_{1.33}Pt₃Ga₈: A modulated variant of the Er₄Pt₉Al₂₄-structure type

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Abstract

Single crystals of Er_{1.33}Pt₃Ga₈ were synthesized in a molten Ga flux. Er_{1.33}Pt₃Ga₈ can be considered to be a modulated variant of the Er₄Pt₉Al₂₄-structure type, where the partial occupancies are ordered. Indeed, the presence of weak satellite reflections indicates a complex organization and distribution of the Er and Ga atoms within the [ErGa] slabs. The structure has been solved based on single crystal X-ray diffraction data in the monoclinic superspace group $X2/m(0\beta0)00$ with a commensurate modulated vector $\mathbf{q}=1/3\mathbf{b}^*$. Precession images also indicate diffusion in the perpendicular direction indicating a partial disorder of this arrangement from layer to layer. In addition, Er_{1.33}Pt₃Ga₈ shows antiferromagnetic ordering at $T_N \sim 5$ K

Keywords

Er_{1.33}Pt₃Ga₈, intermetallics, satellite reflections, modulation, crystal growth, superspace group

1. Introduction

Over the last decade, there has been significant interest in the single crystal growth of highly correlated materials. Ce-based intermetallics, for example, exhibit unusual properties such as magnetically mediated superconductivity, unusual forms of magnetism, and heavy fermion behavior [1, 2]. Er-based intermetallic compounds have been recently gaining interest. For instance, ErPd₂Si₂, a metallic conductor, has been proposed as a new spin model where one incommensurate spin state is attributed to localized spins and a second incommensurate spin state is attributed to itinerant spins [3]. ErPdGa has a collinear antiferromagnetic structure at 1.5 K with a wave vector $k = (0, 1/3, 0)$. At 5 K (the Néel temperature), it then transforms into a sine-wave modulated structure with the wave-vector $k = (0, 0.3804(4), 0)$ [4]. Similar properties were observed in ErPtGa where a sine-modulated structure exists between 1.5 K and 3.2 K [5].

As part of our effort to contribute novel Er-based intermetallics, we have grown single crystals of Er_{1.33}Pt₃Ga₈, which is isostructural to Ln_{1.33}Pt₃Al₈ (Ln = Ce, Gd) [6, 7]. Gd_{1.33}Pt₃Al₈ orders antiferromagnetically at 20 K, but upon doping with silicon to yield Gd_{1.33}Pt₃(Al,Si)₈, the ordering temperature decreases to 7 K [6]. The structures of Ln_{1.33}Pt₃Al₈ (Ln = Ce, Gd) have previously been modeled using space group $R\bar{3}m$ with lattice parameters $a \sim 4.3$ Å and $c \sim 39$ Å. The structure of Er_{1.33}Pt₃Ga₈ is shown in Figure 1 and is composed of two dimensional layers consisting of a Pt₂Al₄ layer, a Ln-Al disordered layer, and a PtAl₂ layer stacked along c -direction, although these layers relative to one another are disordered. Conversely, Er₄Pt₉Al₂₄, which contains the same structural subunits, can be modeled using a lower symmetry monoclinic cell (space group $C2/m$) with lattice parameters $a = 7.462(2)$, $b = 4.31.3(1)$, $c = 13.044(2)$, and $\beta = 100.94(2)^\circ$. This structure was then used as a starting point to model a pseudo-trigonal triclinic cell (space group $P\bar{1}$) with lattice parameters of $a = 7.461(2)$, $b = 7.462(2)$, $c = 13.044(2)$, $\alpha = 90.00(1)$, $\beta = 100.94(2)^\circ$ and $\gamma = 90.13(2)^\circ$ [8]. The difference between the Ln_{1.33}Pt₃Al₈ and Er₄Pt₉Al₂₄ structures results from disorder of stacking along the c -direction between respective layers. Hence, Ln_{1.33}Pt₃Al₈ is described as a disordered variant of Er₄Pt₉Al₂₄, and can be considered an “average structure” with regards to the disorder. Additionally, in Ln₃₃Pt₃Al₈, each

layer has a three-fold axis of symmetry that is aligned with one another along the *c*-direction, preserving the trigonal symmetry throughout the unit cell. This symmetry is broken in $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ due to the layers being staggered resulting in the lower symmetry monoclinic (and triclinic) cell. Regardless, a common property of both phases is the presence of weak, unindexed reflections that are unrelated to the interlayer stacking disorder, but instead originate from the occupational disorder of the Ln-Al layers. However, attempts at solving the supercell structure related to these reflections were unsuccessful.

Intermetallics with structural defects and modulation can lead to charge density waves and unusual magnetism [9] such as spin glass and frustration as seen in SmNiGeAl_4 [10] and SmPd_2Al_3 [5, 6]. REMGa_3Ge (RE = Y, Sm, Gd; M = Co) were found to have complex superstructures occurring in the *ab*-plane, associated with the square net of Ga atoms [11]. Herein, we report the synthesis, the average and modulated crystal structures, and magnetic susceptibility of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$. Weak, unindexed reflections are present similar to $\text{Ln}_{1.33}\text{Pt}_3\text{Al}_8$ and $\text{Er}_4\text{Pt}_9\text{Ga}_{24}$, indicating the presence of a supercell associated with the disordered Er/Ga layer. The structure was solved with these reflections being indexed corresponding to the monoclinic superspace group $X2/m(0\beta0)00$ with a commensurate modulated vector $\mathbf{q}=1/3\mathbf{b}^*$. Precession images also indicate diffusion perpendicular to the direction of the modulation indicating a partial disorder of this arrangement from layer to layer.

2. Experimental

2.1 Synthesis of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$

$\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ crystals were grown using the flux-growth method, which uses a low melting metal as a flux [12, 13]. Er, Pt, and Ga were weighed in a 1.33: 1: 15 ratio and loaded into an alumina crucible. The crucible was placed in a fused-silica tube topped with silica wool. The fused-silica tube and its contents were then evacuated, (< 30 mTorr) flame-sealed, and heated to 1150°C at a rate of 300°C per hour. After dwelling for 7 hours, the vessel was cooled to 350°C at a rate of 8°C/h and spun in a centrifuge to remove excess Ga flux. Hot water was used to separate the aggregate crystals from the gallium flux and 3M DMF/ I_2 solution was employed to clean residual gallium on the surfaces of the single crystals. Cubic and needle-shaped crystals were observed; the needle-shaped crystals were mechanically separated and investigated for this report. The single crystal dimensions were $\sim 0.5 \times 0.5 \times 3 \text{ mm}^3$ [14].

2.2 Single Crystal X-ray Diffraction

Single crystals of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ were cut to suitable sizes for data collection and mounted onto glass fibers with epoxy and collected on a Bruker D8 Quest single crystal X-ray diffractometer equipped with a Mo-target $\text{I}\mu\text{S}$ microfocus X-ray tube ($\lambda = 0.71073 \text{ \AA}$), a HELIOS optics monochromator, and a CMOS detector with range of $\theta = 3.2\text{--}30.4^\circ$. The initial structural models were obtained from direct methods using SHELXTL-2014 and then refined using SHELXL-2014 [15, 16]. The modulated structure refinement has been performed using the JANA2006 software package [17]. Atomic positions, selected interatomic distances, and crystallographic parameters of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ are provided in Tables 1-3 for the average structure and in Tables 4 -5 for the modulated structure.

The structural model of $\text{Gd}_{1.33}\text{Pt}_3\text{Al}_8$, which has been previously reported, was used to perform initial refinements of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ resulting in similar lattice parameters. The observation of unusually large atomic displacement parameters (ADPs) for Er1 and Ga4, however, indicated disorder/partial occupancy, additional ordering, or both. No other ADP values were found to be anomalous, and all refined sites were within $\sim 1\%$ of fully occupied. A residual electron density of $127.24 \text{ e \AA}^{-3}$ and deepest minimum of $-10.00 \text{ e \AA}^{-3}$ were located $\sim 0.03 \text{ \AA}$ and $0.45 \text{ \AA}$ from the Er and Ga4 site, respectively. Thus, occupancies of Er and Ga4 sites were freely refined and found to be ~ 67 and 33% occupancy, respectively. This resulted in excellent statistics ($R \sim 1.5\%$) with the Er1 and Ga4 ADP values decreasing substantially. Nevertheless, unindexed reflections in precession images indicated the presence of a superstructure, which is discussed in Section 3.2.

Table 1. Crystallographic Parameters and Structure Refinement of the Er_{1.33}Pt₃Ga₈ Average Structure

Crystal System	Trigonal
Space Group	$R\bar{3}m$
a (Å)	4.3163(2)
c (Å)	38.547(17)
V (Å ³)	621.93(5)
Z	3
Crystal dimensions (mm ³)	0.01 x 0.02 x 0.05
θ range (°)	3.17 – 30.41
μ (mm ⁻¹)	89.109
Data Collection	
Measured Reflections	7924
Independent Reflections	294
Reflections with $I > 2\sigma(I)$	290
R_{int}	0.0148
h	-6 to 6
k	-6 to 6
l	-54 to 53
Refinement	
R_1 (F) ^a	0.0148
wR_2 ^b	0.0360
Reflections	294
Parameters	27
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	2.013
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-1.560
Extinction coefficient	0.00216(9)
GOF	1.310

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$^b wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}; w = 1/[\sigma^2(F_o^2) + (0.0123 P)^2 + 7.4140 P], [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}.$$

Table 2. Atomic Positions of the Er_{1.33}Pt₃Ga₈ Average Structure in $R\bar{3}m$

Atom	Wyckoff site symmetry	x	y	z	Occ.	$U_{eq} (\text{\AA}^2)^a$
Er	$6c$	0	0	0.26935(1)	0.674(3)	0.0052(2)
Pt1	$3a$	0	0	0	1.00	0.0049(2)
Pt2	$6c$	0	0	0.12014(2)	1.00	0.0054(1)
Ga1	$6c$	0	0	0.44246(3)	1.00	0.0074(2)
Ga2	$6c$	0	0	0.18624(2)	1.00	0.0065(2)
Ga3	$6c$	0	0	0.35301(3)	1.00	0.0053(2)
Ga4	$18h$	0.5382(2)	0.4618(2)	0.39430(4)	0.330(3)	0.0057(5)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Interatomic Distances ($\text{\AA}$) of the Er_{1.33}Pt₃Ga₈ Average Structure in $R\bar{3}m$

Er - Ga1 (x3)	3.0393(7)
Er - Ga3 (x3)	3.0212(7)
Er - Ga4 (x6)	3.088 (1)
Pt1 - Ga3 (x6)	2.6048(3)
Pt1 - Ga4 (x6)	2.539(1)
Pt2 - Ga1 (x3)	2.5280(2)
Pt2 - Ga2 (x1)	2.548(1)
Pt2 - Ga2 (x3)	2.699(1)
Pt2 - Ga4 (x3)	2.4748(15)

2.3 Magnetic Susceptibility

Temperature-dependent susceptibility of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ was measured on a single crystal using a Quantum Design Magnetic Property Measurement System (MPMS) under both field-cooled (FC) and zero-field conditions (ZFC) between 2 and 300 K with an applied magnetic field of 0.1 T.

3. Results and Discussion

3.1 Average Crystal Structure

$\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ can be modeled using space group $R\bar{3}m$ with respective lattice parameters $a = 4.3163(2)$ Å, $c = 38.547(17)$ Å and $V = 621.93(5)$ Å³. This structure is essentially an average structure of the $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ structure, arising from disorder between respective slabs/layers along the c -direction. There are seven crystallographic positions in $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$, including Er, Pt1, Pt2, Ga1-3, and Ga4 occupying the $6c$, $3a$, $6c$, $6c$, and $18h$ sites, respectively. The structure of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$, as shown in Figure 1, is composed of three distinct slabs: $\text{Pt}_2\text{Ga}_4 + 2*[\text{Er}_{0.67}\text{Ga}] + \text{PtGa}_2$ slabs. The slabs stack in the c -direction in an ABCBABC'BA'BC''B sequence, where A is a (Pt_2Ga_4) slab, B is a disordered $\text{Er}_{0.67}\text{Ga}$ slab, and C is a PtGa_2 slab, and the position of the slabs with respect to each other is indicated by A', A''. Similarly, $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ is formed by three distinctive slabs leading to $2 \times [\text{Er}_2\text{Al}_3] + 3 \times [\text{PtAl}_2 + \text{Pt}_2\text{Al}_4]$ that stack in the c -direction. The $\text{Er}_{0.67}\text{Ga}$ slab in $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ can be related to three superimposed Er_2Al_3 slabs in $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ offset by the trigonal cell dimension of $a/\sqrt{3}$ as shown in Figure 2. Due to the partially occupied Ga4 site ($\sim 33\%$) in the $\text{Er}_{0.67}\text{Ga}$ slab, three superimposed Er_2Al_3 slabs must be used to account for the near tripling of the c -dimension of the $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ unit cell.

Figure 1. The unit cell of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ showing different structural units.

Figure 2. The unit cell projections of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ (left) and $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ (right) along the c -axis are shown.

Figure 3. Projection of the $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ crystal structure down the c -axis are shown.

Figure 3 shows the $\text{Er}_{0.67}\text{Ga}$ segment in $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$, which consists of a triangular mesh of partially occupied Ga4 (33 %) atoms with the Er (67 %) atoms residing in the center. When these sites are considered with 100 % occupancy, the Er-Ga distances are 1.536(2) Å and the Ga-Ga distances are 1.663(3) Å for $\text{Er}_{0.67}\text{Ga}$ segments. These distances are too close to be considered as interatomic distances given the sum of Er and Ga atomic radii. Similar contacts of 1.555(9) and 1.5505(5) Å were also found in $\text{Gd}_{1.33}\text{Pt}_3\text{Al}_8$ and $\text{Ce}_{1.33}\text{Pt}_3\text{Al}_8$ [7], respectively. Isostructural analogues $\text{Ln}_{1.33}\text{Pt}_3\text{Al}_8$ ($\text{Ln} = \text{Gd}, \text{Ce}$) [6, 7] also yielded partial occupancy of $\text{Ln} \sim 66$ and $\text{Al} \sim 33$ % where 1/3 of the Ln atoms are exchanged by Al-triangles. An attempt to explain the relationship between the disordered Ln-Al slab and the ordered Ln-Al slab was previously made between $\text{Gd}_{1.33}\text{Pt}_3\text{Al}_8$ and $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ [6]. The partially occupied Gd and Al atoms allow the $\text{GdAl}_{0.67}$ slabs to coincide with each other in the c -direction retaining the 3-fold rotational symmetry, whereas in $\text{Er}_4\text{Pt}_9\text{Al}_{24}$, the Er-Al slabs do not coincide due to the Er and Al being fully occupied and ordered, destroying the 3-fold axis of rotation. The $\text{Ln}_{0.67}\text{X}$ ($\text{Ln} = \text{rare earth}; \text{X} = \text{Al}, \text{Si}, \text{Ga}$) slab is very robust, which is evident in that it has been observed in various

compounds such as $\text{Gd}_{0.67}\text{Pt}_2\text{Al}_5$ [6] and $\text{La}_x\text{Ce}_{1.33-x}\text{Pt}_4\text{Ga}_{10}$ [18], where the Ln atoms are situated in a triangle mesh of X atoms (X = Ga or Al). In the following section it is shown that the partial occupancies of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ are in fact modulated, with a specific ordering of the rare-earth and the Ga atoms within the slab.

There are three distinct Er-Er distances in $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$: one along the *ab*-plane and two along the *c*-direction. The $(\text{Er-Er})_{ab}$ interatomic spacing is 4.316(3) Å, which is comparable to previously reported isostructural analogues $\text{Ln}_{1.33}\text{Pt}_3\text{Al}_8$ (Ln = Gd, Ce) with $(\text{Gd-Gd})_{ab}$ and $(\text{Ce-Ce})_{ab}$ interatomic spacing of 4.3359(6) Å and 4.361(2) Å, respectively. $(\text{Er-Er})_c$ distances are ~ 5.526 Å parted by the PtGa_2 slab; the $(\text{Er-Er})_c$ distances are ~ 8.299 separated by the Pt_2Ga_4 slab. Similarly, $(\text{Gd-Gd})_c$ and $(\text{Ce-Ce})_c$ interatomic distances in $\text{Ln}_{1.33}\text{Pt}_3\text{Al}_8$ (Ln = Gd, Ce) are ~ 5.5486 to 5.5989 and ~ 8.333(1) to 9.4522 Å.

Figure 4 shows the PtGa_2 segment consisting of Pt1, Ga2, and Ga3 and can be described as hexagonal close-packed layers with the Pt atoms residing between the gallium networks. This arrangement has been found in $\text{Y}_2\text{Co}_3\text{Ga}_9$ and isostructural analogs [19-21] as well as $\text{SmNiAl}_4\text{Ge}_2$ [4], $\text{Yb}_2\text{Pd}_3\text{Ga}_9$, [22] CePdGa_6 [2], and $\text{Ce}_2\text{PdGa}_{12}$ [11]. Pt is surrounded by eight gallium atoms (six Ga4 partially occupied (33%) atoms), as shown in Figure 4, with Pt-Ga distances of 2.5386(6) and 2.6048(3) Å, which are slightly greater than the sum of the atomic radii of Ga (1.22 Å) and Pt (1.35 Å) as well as the interatomic distances in Pt-Ga binary compounds, Pt_3Ga [23] and Pt_5Ga_3 [24]. The Pt_2Ga_4 segment consists of Pt2, Ga1, Ga2, and Ga4 forming two PtGa_2 nets that are connected by Ga-Ga bonds. Pt2 is surrounded by a total of eight gallium atoms (three Ga4 partially occupied (33%) atoms), with Pt-Ga distances 2.4748(6) Å, 2.5280(2) Å, 2.5479(1) Å, and 2.6999(4) Å.

Figure 4. The local environment of Pt1 (b) and Pt2 (d) are shown.

3.2 Modulation of Rare Earth and Gallium Occupancies

Precession images of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ in the rhombohedral setting clearly show weak, unindexed reflections occurring between every third main reflection (Figure 5). In order to take into account the weak satellite reflections and to fully describe the structural arrangement, the symmetry has been modified into a monoclinic setting (details regarding the transformation matrix used and the resulting cell can be found in supplementary information) [8]. The modulated structure has been solved using the superspace group $X2/m(0/\beta)00$ (X corresponding to the $(1/2, 1/2, 0, 1/2)$ extra centering) and the lattice parameters $a = 7.4879(2) \text{ \AA}$, $b = 4.3204(3) \text{ \AA}$, $c = 13.1060(4) \text{ \AA}$ with a commensurate modulated vector $\mathbf{q} = 1/3\mathbf{b}^*$.

Figure 5. (a) Precession image of the $(hk0)$ zone (trigonal setting) showing weak, periodic, unindexed reflections indicating modulation. (b) Precession image along the $(h2l)$ direction (monoclinic setting) showing the diffusion/elongation of the reflections related to disorder of stacking between respective slabs.

For further information regarding the modulated structure approach and the use of superspace groups, please refer to Janner et al [25]. The atomic positions refined from the monoclinic average structure, provided in supplementary information, were used as a starting point. As suggested, occupational modulations on the Ga and Er atoms were expected to be the origin of the modulation. Therefore, first order modulation waves (harmonic functions) have been added to describe this trend. This addition drastically improved the quality of the refinement and more accurately described the intensity of the satellite reflections. In a second step, first order modulation waves were added on the atomic positions and atomic displacements for a relative improvement of the refinement. The final refinement converged to a satisfying and overall R of 4.75% with R_{obs} of 2.36 % for the main reflections and R_{obs} of 17.94 % for the satellite reflections. Table 4 provides crystallographic information for the refinement of the modulated structure and Table 5 provides the atomic parameters with the modulated terms for the refinement. Figure 6 illustrates the occupational modulation of the Ga and Er atoms in the [ErGa] layer. The modulation clearly shows Er rich and Er poor regions. Every third unit cell in the site is mostly occupied by Er at ~90% and ~10% of Ga whereas the two neighboring unit

cells are each occupied by Er at ~55% and ~45% of Ga. Again, the observed diffusion suggests that the organization along the perpendicular direction is described by disorder.

A supercell model has been generated from the modulated structure taking into account the commensurability, the satellite reflections, and the choice of t-section (where t-section is defined as the origin in the additional fourth dimension). Details regarding the supercell model can be found in the supplementary information. Although both modulated and supercell models are identical, it is important to note that the supercell model would be difficult to find and refine without the (3+1) D superspace approach as a first step. Moreover, the superspace approach easily describes the change of occupation within the structure (figure 6). Finally, a superspace group also allows one to treat closely related compounds with slight different chemical composition where the modulation is incommensurate.

Table 4. Crystallographic Parameters and Structure Refinement of the $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ Modulated Structure

Formula	$\text{Er}_{0.341}\text{Pt}_{0.75}\text{Ga}_{2.005}$	
Crystal System	Monoclinic	
Superspace Group ^a	$X2/m(0\beta0)00$	
a (Å)	7.4879(2)	
b (Å)	4.3204(3)	
c (Å)	13.1060(4)	
$\mathbf{q}$	$1/3 \mathbf{b}^*$	
t-section/space group	$t_0=0$	$C2/m$
Z	8	
D_x (g cm ⁻³)	10.9526	
R_{over}	4.75%	
R_{main}	2.36%	
$R_{\text{satellites}}$	17.94%	

^aX centering corresponds to the ($1/2$, $1/2$, 0, $1/2$) centering. Supersymmetry elements are listed in the supplementary information.

Table 5. Atomic Parameters with the Modulated Terms for the Refinement of the Er_{1.33}Pt₃Ga₈ Modulated Structure

Atoms	Occupation	Modulation Terms*	x	y	z	U _{eq}
Er1	0.3410(16)		0.26934(12)	0	0.80815(8)	0.0080(3)
		s,1	0	0.0001(3)	0	
		c,1	-0.00040(14)	0	-0.00046(8)	
Pt1	1		0	0	0	0.0063(2)
		s,1	0	0.0037(2)	0	
		c,1	0	0	0	
Pt2	0.5		0.12015(6)	0	0.36045(4)	0.00657(17)
		s,1	0	0.00569(14)	0	
		c,1	-0.00317(8)	0	-0.00053(5)	
Ga2	0.5		0.18637(19)	0	0.55871(12)	0.0076(4)
		s,1	0	-0.0010(4)	0	
		c,1	-0.0004(2)	0	-0.00234(13)	
Ga1_1	0.331(5)		0.3788(14)	0.690(2)	0.8189(6)	0.012(3)
		s,1	-0.0059(16)	0.002(2)	-0.0027(7)	
		c,1	0.006(2)	-0.005(3)	0.0033(10)	
Ga1_2	0.174(4)		-0.0689(19)	0	-0.8180(12)	0.037(7)
		s,1	0	0.0026(9)	0	
		c,1	-0.003(4)	0	-0.003(2)	
Ga3	0.5		-0.14704(19)	0.5	0.05898(12)	0.0068(4)
		s,1	0	-0.0031(4)	0	
		c,1	-0.0025(2)	0	-0.00055(14)	
Ga4	0.5		-0.05762(18)	0.5	0.32728(12)	0.0086(4)
		s,1	0	0.0028(4)	0	
		c,1	0.0012(2)	0	-0.00030(14)	

Occupational Modulated Terms

Atoms	Modulations terms*	Occupation
Er1		0.682(3)
	s,1	0
	c,1	0.225(3)
Ga1_1		0.331(5)
	s,1	0.157(5)
	c,1	-0.195(5)
Ga1_2		0.349(8)
	s,1	0
	c,1	-0.212(11)

ADP Harmonic Parameters and Associated Modulated Terms

Atoms	Mod. Terms*	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Er1		0.0075(5)	0.0067(5)	0.0094(5)	0	0.0006(3)	0
	s,1	0	0	0	-0.0011(5)	0	0.0000(5)
	c,1	-0.0037(5)	-0.0026(5)	-0.0075(5)	0	0.0000(4)	0
Pt1		0.0061(3)	0.0060(3)	0.0064(3)	0	0.0006(2)	0
	s,1	0	0	0	0	0	0
	c,1	0.0003(4)	-0.0002(4)	-0.0001(4)	0	-0.0008(3)	0
Pt2		0.0071(3)	0.0067(3)	0.0056(3)	0	0.0005(2)	0
	s,1	0	0	0	-0.0005(2)	0	0.0003(2)
	c,1	-0.0016(3)	0.0004(3)	0.0013(3)	0	-0.0005(2)	0
Ga2		0.0081(7)	0.0075(7)	0.0071(7)	0	0.0009(5)	0
	s,1	0	0	0	-0.0005(7)	0	-0.0007(7)
	c,1	0.0000(8)	0.0008(9)	-0.0018(8)	0	-0.0032(7)	0
Ga1_1		0.019(6)	0.010(5)	0.008(4)	0.004(4)	0.002(4)	-0.005(3)
	s,1	-0.015(7)	-0.005(6)	-0.001(5)	-0.003(5)	-0.004(5)	0.007(4)
	c,1	0.020(9)	0.005(7)	0.006(7)	0.005(6)	0.003(6)	-0.009(5)
Ga1_2		0.026(10)	0.045(14)	0.030(11)	0	-0.015(8)	0
	s,1	0	0	0	-0.0040(15)	0	-0.0017(15)
	c,1	0.043(19)	0.08(3)	0.05(2)	0	-0.029(15)	0
Ga3		0.0055(6)	0.0052(6)	0.0097(7)	0	0.0014(5)	0
	s,1	0	0	0	-0.0003(6)	0	0.0012(7)
	c,1	-0.0010(8)	-0.0024(9)	-0.0042(9)	0	-0.0010(7)	0
Ga4		0.0064(7)	0.0062(7)	0.0133(8)	0	0.0021(6)	0
	s,1	0	0	0	0.0003(7)	0	-0.0018(7)
	c,1	0.0029(8)	-0.0015(8)	0.0010(9)	0	0.0009(7)	0

*c,1 and s,1 correspond to the cosine and sine functions of the first order of the harmonic modulation, respectively.

Figure 6. (top) Occupational modulated waves vs. t for the Er and Ga1-1 and Ga1-2 atoms. The dash lines represent the commensurate section observed. (bottom) Representation of the commensurate [ErGa] layer showing the waving modulated occupation between the Er and the Ga atomic sites.

3.3 Magnetism

The temperature dependent magnetic susceptibility of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ is shown in Figure 7. An antiferromagnetic transition occurs at 5.7 K and a Curie-Weiss fit to the high-temperature data (150 – 300 K) from $1/\chi$ vs. T yields a $\theta = -1.25$ K with $\mu_{\text{eff}}/\text{Er}^{3+} = 9.59 \mu_{\text{B}}$, in good agreement with the expected value of $9.58 \mu_{\text{B}}/\text{Er}^{3+}$. Compared to $\text{Gd}_{1.33}\text{Pt}_3\text{Al}_8$ ($T_{\text{N}} = 20$ K) [6], $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ has a lower ordering temperature at $T_{\text{N}} = 5.7$ K and follows de Gennes scaling, indicating RKKY interactions facilitate the magnetic coupling between Er moments.

Figure 7. Magnetic susceptibility of $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$ showing a transition at 5.7 K.

4. Conclusions

We report the new compound $\text{Er}_{1.33}\text{Pt}_3\text{Ga}_8$, a modulated variant of the $\text{Er}_4\text{Pt}_9\text{Al}_{24}$ -structure type with the building blocks: PtGa_2 , Pt_2Ga_4 , $\text{Er}_{0.67}\text{Ga}$ slabs. Supercell reflections were observed in the average unit cell initially obtained leading to a lower symmetry monoclinic cell. Here, modulation of the partial occupancies of the erbium and gallium atoms was observed within the disordered RE-Ga slab. Partial displacive disorder along the c -direction exists between layers indicating the bonding between the neighboring layers is weak, allowing for a slight disorder from one layer to another. It is expected that other isostructural analogues also exhibit a similar modulation of the partial occupancies of the rare earth and main group elements.

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Graphical Legend

A precession image of the $hk0$ zone showing weak, periodic, unindexed reflections indicating modulation and representation of the commensurate [ErGa] layer showing the waving modulated occupation