Structural stability and magnetic properties of LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$)

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Abstract: Single crystals of LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) were grown from a Ga self-flux. The compounds crystallize in a “stuffed” variant of the AuCu_3 -structure type where Fe or Co partially occupies the body-centered position of the unit cell surrounded by six Ga atoms. The insertion of Fe or Co guest atoms into the AuCu_3 -structure type causes a structural change in the host material where chemical pressure is exerted on Ga–Ga contacts surrounding the filled octahedra. This in turn affects the stability of the AuCu_3 -structure type and the intrinsic properties of the materials. With increasing Ho–Ho distances of 4.2355(5), 4.2377(5), and 4.2441(3) Å, $\text{HoCo}_{0.16(2)}\text{Ga}_3$, $\text{HoFe}_{0.11(1)}\text{Ga}_3$, and $\text{HoFe}_{0.16(2)}\text{Ga}_3$ order antiferromagnetically with decreasing Néel temperatures of $T_N = 10.2$, 7.2, and 6.5 K, respectively. $\text{ErCo}_{0.06(2)}\text{Ga}_3$, $\text{ErFe}_{0.06(1)}\text{Ga}_3$, and $\text{ErFe}_{0.11(2)}\text{Ga}_3$ order antiferromagnetically with Néel temperatures of $T_N = 3.3$, 5.2, and 6.2 K. The magnetic properties are attributed to changes in the coupling strength of local magnetic moment with conduction electrons as a function of transition metal and rare earth.

Keywords: Intermetallics; Flux Growth; Single Crystal; Magnetism; AuCu_3 -structure type

1. Introduction

The correlation of structure-property relationships for specific applications is highly sought after in materials chemistry research. $\text{Ln}(\text{M},\text{Al})_{12}$ ($\text{Ln} = \text{Y}, \text{Gd-Er}, \text{and Yb}$; $\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{or Cu}$) of the tetragonal ThMn_{12} -structure type is robust and greatly influenced by the selection of lanthanides and transition metals [1,2]. For example, GdCr_4Al_8 orders antiferromagnetically below 7 K [2], while GdCr_6Al_6 [1] and GdFe_6Al_6 [2] order ferromagnetically at 175 K and 345 K (near room temperature!), respectively. $\text{Ln}_4\text{MGA}_{12}$ ($\text{Ln} = \text{Tb-Er}$; $\text{M} = \text{Fe}, \text{Pd}, \text{and Pt}$) crystallizes in the $\text{Y}_4\text{PdGa}_{12}$ -structure type and consists of face-sharing LnGa_3 cuboctahedra with corner-sharing MGA_6 octahedra [3,4]. $\text{Ln}_4\text{PtGa}_{12}$ ($\text{Ln} = \text{Dy-Er}$) exhibits large, positive magnetoresistance up to 50 %, 220 %, and 900 % increase in resistance under an applied magnetic field for Dy, Er, and Ho, respectively [4].

The AuCu_3 -type subunit is found in several of the magnetically mediated superconducting $\text{Ce}_n\text{MIn}_{3n+2}$ ($n = 1, 2$; $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) homologous series and have been reviewed [5,6]. A strategy to change properties of rare earth intermetallics is by the insertion of guest atoms. The AuCu_3 -structure type is of particular interest in our goal to demonstrate how guest atoms in polyhedral subunits can affect the coupling strength of local magnetic moment with conduction electrons, thereby changing the physical properties [7]. Multiple reports indicate that the physical properties of materials are affected when atoms are inserted on to interstitial sites [8-13]. For instance, the hydrogenation of InPd_3 (ZrAl_3 -structure type) yields the hydride $\text{InPd}_3\text{H}_{0.89}$ (AuCu_3 -structure type), where H occupies the octahedral interstitial site [8]. The insertion of nitrogen into the interstitial sites of $(\text{Ln}_3\text{N})\text{In}$ ($\text{Ln} = \text{Sc}, \text{Lu}, \text{and Gd-Tm}$) can also stabilize the AuCu_3 -structure type [9]. LnRh_3B_x ($\text{Ln} = \text{Gd}, \text{Y}, \text{Sc}$) adopts the AuCu_3 -structure type with B occupying the interstitial site [10]. In this series of materials, the room temperature Vickers microhardness is highly dependent on the concentration of boron. Several other examples of crystal structures are also found in literature, including $\text{Yb}_{1-x}\text{Al}_{3-x}\text{Si}_x$ and $\text{Yb}_{1-y}\text{Al}_{3-x}\text{Ge}_x$ [12], TaAl_3 [14] and the “stuffed” ternary variant Pr_3InO [15].

Recently, we have grown single crystals of LnMn_xGa_3 ($\text{Ln} = \text{Ho-Tm}$; $x < 0.2$) adopting the well-known AuCu_3 -structure type with Mn “stuffed” in the octahedral holes [16]. The Ho and Er analogues order antiferromagnetically at 7.7 K and 3.1 K, respectively, with both having slightly higher ordering temperatures than the parent LnGa_3 ($\text{Ln} = \text{Ho}, \text{Er}$) analogues which order at 6.2 K and 2.9 K, respectively [16]. The increase in ordering temperature is attributed to coupling of the local Ln magnetic moments with Mn conduction

electrons. Density functional theory (DFT) chemical pressure analysis was used to study how the interstitial guest atoms change the host system, LnMn_xGa_3 ($\text{Ln} = \text{Ho-Tm}$; $x < 0.2$). Upon the insertion of Mn guest atoms, structural strain is induced on the LnGa_3 gallium sublattice. This structural strain is evident by shorter Ga–Ga contacts and longer Ln–Ln distances in the crystal structure, and is in agreement with DFT calculations [16,17]. Although the Ln–Ln distances are increased relative to the parent compound (which would typically result in a lower ordering temperature), it was proposed that the conduction electrons of the transition metal can mediate Ln–Ln magnetic interactions in compounds with longer Ln–Ln contacts, thus resolving the potential conflict between theory and observation. A recent study has presented the crystal structure and magnetic properties of DyMn_xGa_3 ($x \leq 0.45$) [13]. Similarly to LnMn_xGa_3 ($\text{Ln} = \text{Ho-Tm}$; $x < 0.2$), the crystal structure of DyMn_xGa_3 ($x \leq 0.45$) also adopts the AuCu_3 -structure type with Mn occupying the octahedral interstitial site. The magnetic properties are dependent of the concentration of Mn. Analogous to our work on LnM_xGa_3 , as the concentration of Mn increases for DyMn_xGa_3 ($x \leq 0.45$), the effective magnetic moment (μ_{eff}) gradually decreases from 10.1 to 8.3 μ_B while the Weiss constants increase from 32 to 91 K [13]. This change in the effective magnetic moment correlates to variations in structural features found in the crystal structure of DyMn_xGa_3 ($x \leq 0.45$), particularly the Mn–Ga/Dy interatomic distances and angles of the MnGa_6 and MnDy_8 coordination polyhedra [13].

The structural changes of LnGa_3 ($\text{Ln} = \text{Ho-Tm}$) upon insertion of Mn has led to the investigation of inserting other transition metals such as iron and cobalt. However, insertion of the transition metal into the parent structure can be difficult to resolve low concentrations and small structural changes; therefore, it is important to grow single crystals for this structural investigation. In this manuscript, we report the synthesis, crystal structure, and magnetic properties of LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$).

2. Methods and Materials

2.1. Synthesis

Single crystals of LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) were grown from their constituent elements via the flux growth method. For this technique, a low melting metal, such as gallium, can be used as the flux which enables metals with higher melting points to dissolve at relatively lower temperatures [6,18-20]. Ln ($\text{Ln} = \text{Ho, Er}$; rods, 99 %), M ($\text{M} = \text{Fe, Co}$; powder, 99.9 %), and Ga (shot, 99.9 %) were used as received. Ln:M:Ga were placed in an alumina crucible with atomic ratios of 1:0.1:20 and 1:0.2:20, topped with a second

inverted alumina crucible containing quartz wool, backfilled with $\sim 1/3$ atm of Ar, and sealed in a fused silica tube. The sealed vessels were then heated to 1150 °C at a rate of 100 °C/h and for 5 hours, cooled to 550 °C at a rate of 5 °C/h, and finally cooled to 300 °C at a rate of 100 °C/h. Samples were then removed from the furnace and centrifuged in order to separate the excess Ga flux. Residual Ga flux on the surface of the single crystals was removed by repeated sonication in hot water. The synthetic procedure resulted in single crystals ranging between 2 – 5 mm³, as shown in Figure 1. The reactions of Ln:Co:Ga (Ln = Ho, Er) with ratios 1:0.2:20 led to undesirable binaries and small amounts of Ln₂CoGa₈ (Ln = Ho, Er), which was identified by elemental analysis and single crystal X-ray diffraction. Reactions with higher concentrations ($x > 0.2$) of Fe produce Ln₄FeGa₁₂ (Ln = Ho, Er) [3].

Figure 1. Ingot as grown via flux growth methods of HoFe_{0.11(1)}Ga₃.

2.2. Elemental Analysis

Single crystals of LnM_xGa₃ (Ln = Ho, Er; M = Fe, Co) were characterized by [energy-dispersive X-ray spectroscopy](#) (EDS) using a LEO 1530 VP SEM equipped with an EDAX detector operated with an accelerating voltage of 19 kV. Multiple polished crystals from each batch were examined. Spectra were integrated for 30 seconds, the results from 5 spots on the single crystal were averaged, and atomic ratios were normalized to the lanthanide. The elemental compositions of samples are as follows: Ho_{1.00(4)}Fe_{0.14(1)}Ga_{2.94(6)}, Ho_{1.00(1)}Fe_{0.16(2)}Ga_{2.97(1)}, and Ho_{1.00(1)}Co_{0.24(2)}Ga_{3.03(2)}, Er_{1.00(6)}Fe_{0.08(1)}Ga_{2.27(7)}, Er_{1.00(1)}Fe_{0.11(1)}Ga_{2.91(1)}, Er_{1.00(1)}Co_{0.14(1)}Ga_{3.06(1)}. Despite the slight disagreement between the refined model of single crystal X-ray diffraction data and the EDS data, the results indicate a systematic incorporation of transition metals into the AuCu₃-structure type. We attribute this compositional variation to the semiquantitative nature of the EDS measurements.

2.3. Structure Determination

Powder X-ray diffraction data was collected on ground single crystals of LnM_xGa₃ (Ln = Ho, Er; M = Fe, Co; $x < 0.2$) using a Bruker D8 Advance powder X-ray diffractometer equipped with a LYNXEYE XE detector using a Cu K α_1 radiation source ($\lambda = 1.54184$ Å).

The reflections were indexed to the AuCu_3 -structure type with a consistent increase in unit cell dimensions upon insertion of guest metal atoms. Single crystal fragments of LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) were cut into suitable sizes and mounted on glass fibers with epoxy. Data sets were collected on a Bruker D8 Quest Kappa single crystal X-ray diffractometer equipped with an I μ S microfocus Mo $\text{K}\alpha_1$ radiation source ($\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 1 mA. Each data set was indexed to a primitive cubic cell with dimension $a \sim 4.25 \text{ \AA}$. There were no additional reflections in the single crystal X-ray diffraction data suggesting supercell ordering. Initial models of the crystal structure were first obtained using SIR2008 [21] and refined using SHELXL2014 [22]. Several models were considered for this system to best represent the crystal structure chemically. The best model shows the M site as partially occupied and models the Ga atoms to occupy either the Ga site (when there is no M atom present) or the Ga' site (when there is a M atom present). It should be noted that the data to parameter ratio is low for these refinements. This stems from the low number of unique reflections and not from excessive use of parameters to fit the data. The single crystal X-ray diffraction data collection and refinement parameters for LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) are provided in Tables 1 and 2 for the Ho and Er analogues, respectively. The atomic positions, Wyckoff site symmetries, displacement parameters, and site occupancies for the Ho and Er samples are given in Tables 3 and 4, respectively. Tables 5 and 6 provide selected interatomic distances for the Ho and Er analogues, respectively.

Table 1. Crystallographic data and refinement parameters of HoM_xGa_3 ($\text{M} = \text{Fe}, \text{Co}; x < 0.2$)

Formula	$\text{HoFe}_{0.11(1)}\text{Ga}_3$	$\text{HoFe}_{0.16(2)}\text{Ga}_3$	$\text{HoCo}_{0.16(2)}\text{Ga}_3$
Space group	$Pm\bar{3}m$	$Pm\bar{3}m$	$Pm\bar{3}m$
a (Å)	4.2377(5)	4.2441(3)	4.2355(5)
V (Å ³)	76.10(3)	76.45(2)	75.98(3)
Z	1	1	1
Crystal size (mm ³)	0.03 x 0.04 x 0.07	0.04 x 0.06 x 0.08	0.04 x 0.06 x 0.10
θ Range (°)	4.81 - 30.21	4.80 - 30.16	4.81 - 30.23
μ (mm ⁻¹)	56.224	52.14	53.70
Collected reflections	734	1648	745
Unique reflections	41	41	40
R_{int}	0.057	0.041	0.052
h	$-5 \leq h \leq 5$	$-6 \leq h \leq 5$	$-4 \leq h \leq 6$
k	$-5 \leq k \leq 5$	$-5 \leq k \leq 5$	$-4 \leq k \leq 5$
l	$-6 \leq l \leq 5$	$-5 \leq l \leq 6$	$-4 \leq l \leq 5$
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	1.12	0.56	1.36
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.64	-1.21	-1.81
GoF	1.19	1.55	1.26
Extinction coefficient	0.22(3)	0.065(5)	0.11(3)
^a $R_I(F)$ for $F_o^2 > 2\sigma(F_o^2)$	0.011	0.012	0.025
^b $wR_2(F_o^2)$	0.025	0.019	0.052

$$^a R_I = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table 2. Crystallographic parameters of ErM_xGa_3 ($\text{M} = \text{Fe}, \text{Co}; x < 0.2$)

Formula	$\text{ErFe}_{0.06(1)}\text{Ga}_3$	$\text{ErFe}_{0.11(2)}\text{Ga}_3$	$\text{ErCo}_{0.06(2)}\text{Ga}_3$
Space group	$Pm\bar{3}m$	$Pm\bar{3}m$	$Pm\bar{3}m$
a (Å)	4.2227(9)	4.2263(10)	4.2201(15)
V (Å ³)	75.30(5)	75.49(5)	75.16(8)
Z	1	1	1
Crystal size (mm ³)	0.04 x 0.04 x 0.12	0.04 x 0.04 x 0.10	0.02 x 0.04 x 0.06
θ Range (°)	4.83 - 30.33	4.82 - 30.30	4.83 - 30.35
μ (mm ⁻¹)	58.423	58.274	59.223
Collected reflections	734	756	745
Unique reflections	41	41	41
R_{int}	0.055	0.058	0.036
h	$-4 \leq h \leq 6$	$-6 \leq h \leq 4$	$-5 \leq h \leq 5$
k	$-5 \leq k \leq 5$	$-5 \leq k \leq 5$	$-5 \leq k \leq 5$
l	$-6 \leq l \leq 5$	$-5 \leq l \leq 6$	$-5 \leq l \leq 4$
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.90	1.01	1.31
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.68	-1.87	-1.22
GoF	1.20	1.27	1.53
Extinction coefficient	0.17(2)	0.20(4)	—
^a $R_I(F)$ for $F_o^2 > 2\sigma(F_o^2)$	0.010	0.018	0.022
^b $wR_2(F_o^2)$	0.022	0.039	0.053

$$^a R_I = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table 3. Atomic positions of HoM_xGa_3

	Wyckoff Site	Point Symmetry	x	y	z	Occupancy	U_{eq}/U_{iso} ($\text{\AA}^2$)
HoFe_{0.11(1)}Ga₃							
Ho	1a	$m\bar{3}m$	0	0	0	1	0.0080(6)
Fe	1b	$m\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.105(10)	0.004(5)
Ga	3c	4/ <i>mm.m</i>	0	$\frac{1}{2}$	$\frac{1}{2}$	0.74(2)	0.0105(11)
Ga'	6f	4 <i>m.m</i>	0.059(12)	$\frac{1}{2}$	$\frac{1}{2}$	0.163(12)	0.0105(11)
HoFe_{0.16(2)}Ga₃							
Ho	1a	$m\bar{3}m$	0	0	0	1	0.00642(19)
Fe	1b	$m\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.161(8)	0.009(3)
Ga	3c	4/ <i>mm.m</i>	0	$\frac{1}{2}$	$\frac{1}{2}$	0.65(5)	0.009(4)
Ga'	6f	4 <i>m.m</i>	0.068(11)	$\frac{1}{2}$	$\frac{1}{2}$	0.18(2)	0.009(4)
HoCo_{0.16(2)}Ga₃							
Ho	1a	$m\bar{3}m$	0	0	0	1	0.0088(9)
Co	1b	$m\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.17(2)	0.015(7)
Ga	3c	4/ <i>mm.m</i>	0	$\frac{1}{2}$	$\frac{1}{2}$	0.60(8)	0.0113(18)
Ga'	6f	4 <i>m.m</i>	0.063(8)	$\frac{1}{2}$	$\frac{1}{2}$	0.22(4)	0.0113(18)

The Ga and Ga' sites are refined isotropically, except for HoFe_{0.16(2)}Ga₃ where they are refined anisotropically.

Table 4. Atomic positions of ErM_xGa₃

	Wyckoff Site	Point Symmetry	x	y	z	Occupancy	U_{eq}/U_{iso} ($\text{\AA}^2$)
ErFe_{0.06(1)}Ga₃							
Er	1a	$m\bar{3}m$	0	0	0	1	0.0082(4)
Fe	1b	$m\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.062(8)	0.005(7)
Ga	3c	4/ <i>mm.m</i>	0	$\frac{1}{2}$	$\frac{1}{2}$	0.78(4)	0.0110(8)
Ga'	6f	4 <i>m.m</i>	0.062(6)	$\frac{1}{2}$	$\frac{1}{2}$	0.15(2)	0.0110(8)
ErFe_{0.11(2)}Ga₃							
Er	1a	$m\bar{3}m$	0	0	0	1	0.0035(8)
Fe	1b	$m\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.106(18)	0.002(8)
Ga	3c	4/ <i>mm.m</i>	0	$\frac{1}{2}$	$\frac{1}{2}$	0.68(5)	0.0061(15)
Ga'	6f	4 <i>m.m</i>	0.066(6)	$\frac{1}{2}$	$\frac{1}{2}$	0.18(3)	0.0061(15)
ErCo_{0.06(2)}Ga₃							
Er	1a	$m\bar{3}m$	0	0	0	1	0.0035(10)
Co	1b	$m\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.06(2)	0.02(3)
Ga	3c	4/ <i>mm.m</i>	0	$\frac{1}{2}$	$\frac{1}{2}$	0.85(3)	0.0090(10)
Ga'	6f	4 <i>m.m</i>	0.088(14)	$\frac{1}{2}$	$\frac{1}{2}$	0.06(2)	0.0090(10)

The Ga and Ga' sites are refined isotropically

Table 5. Selected interatomic distances (Å) for HoM_xGa_3 (M = Fe, Co)

Interatomic distance	HoFe_{0.11(1)}Ga₃	HoFe_{0.16(2)}Ga₃	HoCo_{0.16(2)}Ga₃
Ln-Ga (x12)	2.9965(3)	3.0010(2)	2.9950(4)
Ln-Ga' (x12)	3.0050(4)	3.01(5)	3.007(3)
Ln-M (x8)	3.6700(2)	3.67(5)	3.6681(3)
M-Ga (x6)	2.1188(2)	2.1221(1)	2.1178(3)
M-Ga' (x6)	2.428(16)	1.83(4)	2.38(3)

Table 6. Selected interatomic distances (Å) for ErM_xGa_3 (M = Fe, Co)

Interatomic distance	ErFe_{0.06(1)}Ga₃	ErFe_{0.11(2)}Ga₃	ErCo_{0.06(2)}Ga₃
Ln-Ga (x12)	2.9859(6)	2.9884(7)	2.9841(11)
Ln-Ga' (x12)	2.997(2)	3.002(8)	3.007(8)
Ln-M (x8)	3.6570(2)	3.6601(3)	3.6547(4)
M-Ga (x6)	2.1113(4)	2.1131(5)	2.1100(8)
M-Ga' (x6)	2.37(2)	2.39(3)	2.48(6)

2.4. Physical Properties

Single crystals of LnM_xGa_3 (Ln = Ho, Er; M = Fe, Co; $x < 0.2$) were selected for magnetic measurements. Magnetization for crystals of LnM_xGa_3 (Ln = Ho, Er; M = Fe, Co; $x < 0.2$) were measured on a Quantum Design Magnetic Property Measurement System (MPMS) outfitted with a Superconducting Quantum Interference Device (SQUID). The temperature dependent magnetization experiments were conducted from 2 K to 300 K with an applied field of 0.01 T, with the exception of $\text{HoFe}_{0.16}\text{Ga}_3$, which was measured with an applied field of 0.1 T. The field-dependence magnetization experiments were measured at 3 K with applied fields up to 7 T.

3. Results and Discussion

3.1. Crystal Structure

LnM_xGa_3 (Ln = Ho, Er; M = Fe, Co; $x < 0.2$) is best modeled using the cubic space group $Pm\bar{3}m$ where $a \sim 4.2$ Å. The crystal structure of $\text{ErFe}_{0.06(1)}\text{Ga}_3$ is shown in Figure 2 as a representative of all the reported analogues. The structure of $\text{ErFe}_{0.06(1)}\text{Ga}_3$ consists of face sharing ErGa_3 cuboctahedra with Er–Ga interatomic distances of 2.9859(6) Å. The crystal structure can be described as a stuffed variant of the AuCu_3 -structure type with the lanthanide

atoms occupying the $1a$ site at the corners of the unit cell, while the Fe atom partially occupies the $1b$ site at the body-centered position of the unit cell, as shown in Figure 2. Fe occupies the body-centered position forming an octahedron with $\text{Fe}-\text{Ga}'$ interatomic distances of $2.37(2)$ Å (Tables 5 and 6). The $\text{M}-\text{Ga}$ distances reported here are comparable to those found in $\text{Ln}_4\text{MGa}_{12}$ ($\text{Ln} = \text{Tb}-\text{Er}$; $\text{M} = \text{Cr}, \text{Fe}$) with M residing in the body centered position [3,6,23,24].

As a result of Fe or Co insertion, the electron density associated with the Ga atoms become prolated (demonstrated in Figure 2a), suggesting that the site is better modeled as split between two crystallographic positions. This model is also chemically reasonable; it shows that when a transition metal is present in a given unit cell, it induces negative chemical pressure which forces the Ga atoms from the typical $3c$ site to a $6f$ site in order to alleviate the strain. The authors have previously reported a detailed discussion for the splitting of the Ga position in the isostructural LnMn_xGa_3 ($\text{Ln} = \text{Ho}-\text{Tm}$; $x < 0.2$) [7]. Similar splitting of a Ga site was used in $\text{Er}_4\text{Fe}_{0.67}\text{Ga}_{12}$ of the $\text{Y}_4\text{PdGa}_{12}$ -structure type, where two gallium positions were observed on the unit cell faces [3].

Figure 2. (a) Unit cell of $\text{ErFe}_{0.06(1)}\text{Ga}_3$ with the elongated Ga site. (b) Unit cell of $\text{ErFe}_{0.06(1)}\text{Ga}_3$ with the split Ga and Ga' sites and partially occupied transition metal site. (c) Crystal packing found in $\text{ErFe}_{0.06(1)}\text{Ga}_3$. Er, Ga, and Fe atoms are represented in grey, blue and orange, respectively. Hatched spheres indicate partial occupancy.

For comparison, the parent analogue ErGa_3 has lattice parameters of $a = 4.2149(10)$ Å, while $\text{ErMn}_{0.041}\text{Ga}_3$ and $\text{ErMn}_{0.118}\text{Ga}_3$ have slightly larger dimensions of $a = 4.2303(3)$ Å and $a = 4.2351(2)$ Å, respectively [16]. The incorporation of Fe and Co into ErM_xGa_3 ($\text{M} = \text{Fe}, \text{Co}$; $x < 0.2$) has led to comparable unit cell dimensions of $a = 4.2227(9)$, $a = 4.2263(10)$, and $a = 4.2201(15)$ Å for $\text{ErFe}_{0.06(1)}\text{Ga}_3$, $\text{ErFe}_{0.11(2)}\text{Ga}_3$, and $\text{ErCo}_{0.06(2)}\text{Ga}_3$, respectively. The increase in unit cell occurs as the concentration of the guest metal atoms increase. This increasing unit cell trend is also observed in the HoM_xGa_3 ($\text{M} = \text{Fe}, \text{Co}$; $x < 0.2$) analogues.

3.2. Magnetization

The temperature dependent magnetic susceptibility of HoM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) and ErM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) are shown in Figure 3. All compounds display Curie-Weiss behavior at temperatures above 70 K. The magnetic susceptibility of LnM_xGa_3 ($\text{Ln} = \text{Er}, \text{Ho}; M = \text{Fe}, \text{Co}; x < 0.2$) were fit to the Curie-Weiss equation, $\chi = \chi_0 + (C/(T-\theta))$, where χ_0 is the temperature independent contribution, θ is the Weiss constant, and C is the Curie constant and are provided in Table 7.

Figure 3. Temperature dependent magnetic susceptibility of single crystalline HoM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) (left) and ErM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) (right). Néel temperatures (T_N) are also denoted for each analogue.

Table 7. Magnetic parameters for single crystal LnM_xGa_3 ($\text{Ln} = \text{Ho}, \text{Er}; M = \text{Fe}, \text{Co}; x < 0.2$)

Compound	T_N (K)	Fit Range (K)	θ_w (K)	μ_{eff} (μ_B/Ln)
$\text{HoFe}_{0.11(1)}\text{Ga}_3$	7.2	40 – 185	-20.2(5)	11.7
$\text{HoFe}_{0.16(2)}\text{Ga}_3$	6.5	40 – 185	-19.9(3)	10.6
$\text{ErFe}_{0.06(1)}\text{Ga}_3$	5.2	70 – 300	-10.43(5)	10.8
$\text{ErFe}_{0.11(2)}\text{Ga}_3$	6.2	70 – 300	-8.24(8)	10.4
$\text{HoCo}_{0.16(2)}\text{Ga}_3$	10.2	70 – 300	-12.42(8)	10.8
$\text{ErCo}_{0.06(2)}\text{Ga}_3$	3.3	70 – 300	-6.41(5)	10.1

$$\text{Ho}^{3+} \mu_{\text{calc}} = 10.61 \mu_B, \text{Er}^{3+} \mu_{\text{calc}} = 9.58 \mu_B.$$

Figure 4. Field dependent magnetization of HoM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) (left) and ErM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) (right) collected at 3 K.

The effective moments (μ_{eff}) of HoM_xGa_3 are ($M = \text{Fe}, \text{Co}; x < 0.2$) 11.7, 10.6, and $10.8 \mu_{\text{B}}/\text{mol Ho}$ for $\text{HoFe}_{0.11(1)}\text{Ga}_3$, $\text{HoFe}_{0.16(2)}\text{Ga}_3$, and $\text{HoCo}_{0.16(2)}\text{Ga}_3$, respectively. The magnetic moments of the Ho analogues presented here are similar to the moments of the hexagonal $\beta\text{-HoGa}_3$ ($\beta\text{-HfNi}_3$ -structure type, $10.7(1) \mu_{\text{B}}/\text{mol}$), cubic $\text{HoMn}_{0.077(11)}\text{Ga}_3$ (AuCu_3 -structure type, $10.616(4) \mu_{\text{B}}/\text{mol}$), and cubic $\text{HoMn}_{0.152(10)}\text{Ga}_3$ (AuCu_3 -structure type, $10.15(1) \mu_{\text{B}}/\text{mol}$). [16,25]. More importantly, the magnitude of the Weiss temperatures, which for HoM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) presented here, are dependent on identity of the transition metal. The Weiss temperatures are comparable with those reported for the $\text{HoMn}_{0.077(11)}\text{Ga}_3$ and $\text{HoMn}_{0.152(10)}\text{Ga}_3$ with $\theta = -17.26(5) \text{ K}$ and $-7.56(12) \text{ K}$ [16]. $\text{HoFe}_{0.11(1)}\text{Ga}_3$, $\text{HoFe}_{0.16(2)}\text{Ga}_3$, and $\text{HoCo}_{0.16(2)}\text{Ga}_3$ order antiferromagnetically at $T_{\text{N}} \sim 7.2, 6.5$, and 10.2 K , respectively with transition temperatures decreasing with increasing Fe concentration unlike the ErFe_xGa_3 ($x < 0.2$) analogues, as seen in Figure 5. The $\text{HoCo}_{0.16(2)}\text{Ga}_3$ has the highest ordering temperature of all analogues (10.2 K) due to the closest Ho-Ho contacts.

The field-dependent magnetization data at 3 K of HoM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) is shown in Figure 4. The field dependent magnetization for both Fe-containing Ho analogues displays field dependent behavior with no signs of saturation up to 7 T. However, the Co analogue only displays a linear dependence as a function of field at low fields but saturates above 4 T.

The effective moments (μ_{eff}) of ErM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) are 10.8, 10.4, and $10.1 \mu_{\text{B}}/\text{mol Er}$ for $\text{ErFe}_{0.06(1)}\text{Ga}_3$, $\text{ErFe}_{0.11(2)}\text{Ga}_3$, and $\text{ErCo}_{0.06(2)}\text{Ga}_3$, respectively and higher than a free Er^{3+} ion ($\mu_{\text{calc}} = 9.58 \mu_{\text{eff}}$). This increase in effective moment is attributed to the

addition (or “stuffing”) of magnetic transition metal atoms into the interstitial site of the structure with Fe possibly carrying a magnetic moment. The Weiss constants are also affected by Fe concentration and similar to the previously reported ErMn_xGa_3 ($x < 0.15$) and DyMn_xGa_3 ($x < 0.45$) [13,16]. $\text{ErFe}_{0.06(1)}\text{Ga}_3$, $\text{ErFe}_{0.11(2)}\text{Ga}_3$, and $\text{ErCo}_{0.06(2)}\text{Ga}_3$ order antiferromagnetically at $T_N \sim 5.2, 6.2$, and 3.3 K, respectively, and slightly higher to the 2.9 K antiferromagnetic ordering temperature of ErGa_3 . The constants obtained from the Curie-Weiss fit suggest several effects of the guest atom. With increasing Fe-concentration, the Weiss constant is slightly reduced. However, the ordering temperature of the Fe-containing Er analogues increases as the concentration of Fe increases. This suggests that the additional conduction electrons are playing a key role in the magnetic properties of the material. The Co-containing analogue has a smaller effective magnetic moment ($10.1 \mu_B/\text{Er}$), Weiss constant ($-6.41(5)$ K, and ordering temperature (3.3 K). The field-dependent magnetization of ErM_xGa_3 ($M = \text{Fe}, \text{Co}; x < 0.2$) measured at 3 K is linear at low fields followed by a curvature at ~ 2 T and does not saturate.

Figure 5. Néel temperatures as a function of Ln–Ln distance for LnM_xGa_3 ($\text{Ln} = \text{Ho–Tm}; M = \text{Mn–Co}, x < 0.2$). Data for ErGa_3 , TmGa_3 and Mn analogues were obtained from previous work [16].

4. Conclusions

Single crystals of LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) have been grown using the flux growth method and characterized by single crystal X-ray diffraction. It was found that when Fe or Co atoms are present, these materials adopt a “stuffed” variant of the AuCu_3 -structure type where the Fe or Co guest atoms partially occupy the body centered position of the unit cell. This induces a negative chemical pressure on neighboring gallium atoms that cause them to displace into adjacent void spaces. The magnetic parameters of LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) display subtle changes as the concentration of guest atoms change.

The trends presented here as summarized in Figure 5 are attributed to the Ln–Ln interatomic distances as a function of guest atom concentration. LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) order antiferromagnetically at higher temperatures than the parent analogues ($T_N \sim 2.9$ K and 6.2 K for ErGa_3 and HoGa_3 , respectively). Substitution of the rare earth or transition metal can affect the coupling of f -electrons, thereby influencing the magnetic coupling strength. The change in Ln–Ln distances in LnM_xGa_3 ($\text{Ln} = \text{Ho, Er}$; $\text{M} = \text{Fe, Co}$; $x < 0.2$) is clearly influencing coupling strength which leads to a change in magnetic ordering temperatures. The design strategy has clearly been demonstrated not only in LnMn_xGa_3 ($\text{Ln} = \text{Ho–Tm}$; $x < 0.15$) and DyMn_xGa_3 ($x < 0.45$), but also in the transition metal analogues as reported herein.

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References

1. I. Felner, M. Seh, and I. Nowik, *J. Phys. Chem. Solids* 42 (1981) 1091.
2. I. Nowik, I. Felner, and M. Seh, *J. Magn. Magn. Mater.* 15 (1980) 1215.
3. B.L. Drake, F. Grandjean, M.J. Kangas, E.K. Okudzeto, A.B. Karki, M.T. Sougrati, D.P. Young, G.J. Long, and J.Y. Chan, *Inorg. Chem.* 49 (2009) 445.
4. J.Y. Cho, M. Moldovan, D.P. Young, and J.Y. Chan, *J. Phys.: Condens. Matter* 19 (2007) 266224.
5. R.T. Macaluso, J.L. Sarrao, N.O. Moreno, P.G. Pagliuso, J.D. Thompson, F.R. Fronczek, M.F. Hundley, A. Malinowski, and J.Y. Chan, *Chem. Mater.* 15 (2003) 1394.
6. W.A. Phelan, M.C. Menard, M.J. Kangas, G.T. McCandless, B.L. Drake, and J.Y. Chan, *Chem. Mater.* 24 (2012) 409.
7. D.C. Schmitt, B.L. Drake, G.T. McCandless, and J.Y. Chan, *Acc. Chem. Res.* 48 (2015) 612.

8. H. Kohlmann, A.V. Skripov, A.V. Soloninin, and T.J. Udovic, *J. Solid State Chem.* 183 (2010) 2461.
9. M. Kirchner, W. Schnelle, F.R. Wagner, and R. Niewa, *Solid State Sci.* 5 (2003) 1247.
10. T. Shishido, J. Ye, K. Kudou, S. Okada, K. Obara, T. Sugawara, M. Oku, K. Wagatsuma, H. Horiuchi, and T. Fukuda, *J. Alloys Compd.* 291 (1999) 52.
11. C. Allio and B. Harbrecht, *Dalton Trans.* (2006) 5352.
12. J.-T. Zhao, W. Schnelle, and Y. Grin, *J. Solid State Chem.* 163 (2002) 113.
13. N. Belyavina, O. Nakonechna, M. Babich, and V. Markiv, *J. Alloys Compd.* 643 (2015) 137.
14. C.L. Condon, G.J. Miller, J.D. Strand, S.L. Bud'k, and P.C. Canfield, *Inorg. Chem.* 42 (2003) 8371.
15. A.D. Christianson and S. Bobev, *Acta Crystallogr. Sect. E: Struct. Rep. Online* 63 (2007) i184.
16. B.W. Fulfer, J.D. McAlpin, J. Engelkemier, G.T. McCandless, J. Prestigiacomo, S. Stadler, D.C. Fredrickson, and J.Y. Chan, *Chem. Mater.* 26 (2013) 1170.
17. J. Engelkemier, V.M. Berns, and D.C. Fredrickson, *J. Chem. Theory Comput.* 9 (2013) 3170.
18. P.C. Canfield and Z. Fisk, *Philos. Mag. A* 65 (1992) 1117.
19. M.G. Kanatzidis, R. Pöttgen, and W. Jeitschko, *Angew. Chem. Int. Ed.* 44 (2005) 6996.
20. E.L. Thomas, J.N. Millican, E.K. Okudzeto, and J.Y. Chan, *Comments Inorg. Chem.* 27 (2006) 1.
21. M.C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, and R. Spagna, *J. Appl. Crystallogr.* 40 (2007) 609.
22. G. Sheldrick, *Acta Crystallogr., Sect. C* 71 (2015) 3.
23. L.O. Vasilenko, A.S. Noga, Y.N. Grin, M.D. Koterlin, and Y.P. Yarmolyuk, *Russ. Metall.* 5 (1988) 216.
24. B.R. Slater, H. Bie, S.S. Stoyko, E.D. Bauer, J.D. Thompson, and A. Mar, *J. Solid State Chem.* 196 (2012) 409.
25. A. Czopnik, *Phys. Status Solidi A* 147 (1995) K35.