SUPPORTING INFORMATION

Magnesium Substitutions in Rare-Earth Metal Germanides with the Orthorhombic Gd_5Si_4-type Structure. Synthesis, Crystal Chemistry and Magnetic Properties of $RE_{5-x}Mg_xGe_4$ (RE = Gd-Tm, Lu and Y)

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Additional experimental results

All manipulations involving the pure elements (purchased from Alfa or Ames Laboratory with purity greater than 99.9% metal basis, used as received), were performed inside an argon-filled glove-box or under vacuum. Below, we provide a summary of the typical experiments.

1. Stoichiometric reactions in welded Nb containers. These reactions were carried out by loading the corresponding elements in the desired stoichiometric ratios and sealing them in 3/8" Nb-tubes under Ar atmosphere. Initially, eight syntheses were undertaken with the ratio *RE* : Mg : Ge = 4 : 1 : 4 (*RE* = Gd-Tm, Lu, Y), modeled after the previously described $Yb_{5-x}Mg_xGe_4$ ($x \approx 1.0$-1.2).[Tobash, P. H.; Bobev, S. *J. Am. Chem. Soc*. **2006**, *128*, 3532] Since structural work suggested that the resultant $RE_{5-x}Mg_xGe_4$ phases had different *RE* and Mg ratios, new reactions were set up with the nominal composition matching that obtained from the single-crystal refinements. In both cases, the heating profile consisted of five segments: i) heating to 1373 K at a rate of 200°/h; ii) 20 hours homogenization period at 1373 K, followed by iii), a quick drop of temperature to 973 K (rate 100°/h). In order to improve the crystallinity, the fourth step involved a long (20 days) annealing at 973 K. Lastly, the annealed samples were cooled to room temperature over the course of one day. Although virtually all of these reactions yielded small, irregularly-shaped crystals of the title compounds, which were suitable for single-crystal X-ray diffraction studies, there were small amounts of side products as well. The known phases RE_2MgGe_2 [(a) Choe, W.; Miller, G.; Levin, E. *J. Alloys Compd*. **2001**, *329*, 121. (b) Kraft, R.; Pöttgen, R. *Montash. Chem*. **2004**, *135*, 1327] RE_3Ge_4 [Tobash, P. H.; DiFilippo, G.; Bobev, S.; Hur, N.; Thompson, J. D.; Sarrao, J. L. *Inorg. Chem*. **2007**, *46*, 8690], RE_5Ge_3 and *RE*Ge [Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed.; American Society for Metals: Materials Park, OH, 1991] were the most recurring ones.

To mitigate this problem, other synthetic strategies were sought. Increasing the reaction temperature proved a viable route towards $RE_{5-x}Mg_xGe_4$ as a single-phase product. For example, high-quality samples

for magnetization measurements were synthesized in quantitative yields by weighing the elements in the ratio *RE* : Mg : Ge = 3.5 : 1.5 : 4 (chosen to be in the middle of the presumed phase range), sealing them in tubes and running the reactions at 1553 K for 2 hours, followed by fast cooling fast – with or without annealing. In spite of the successful application of this method, the benefits of the high reaction temperature were frequently offset by unwanted side reactions with the Nb-container, posing a serious safety issue. With that regard, the more expensive and more robust Ta might prove better suited for such applications.

2. Reactions with excess Mg. This was done with the idea to probe the limit of the homogeneity range of the $RE_{5-x}Mg_xGe_4$ phases. For this purpose, Mg was loaded with 2-, 3-, and 5-fold excess, while keeping the *RE* : Ge ratio constant. To reduce the risk of pressure built-up in the welded Nb ampoules (due to the high vapor pressure of Mg (b.p. 1363 K)), the reactions were subjected to the following treatment: i) heating to 1273 K at a rate of 200°/h; ii) 1.5 hours homogenization at 1273 K; and iii) cooling at a rate of 20°/h. These reactions afforded mixtures of known binary (e.g. Mg_2Ge, RE_3Ge_4, $REGe_{2-x}$) and ternary phases (RE_2MgGe_2) as major products; the desired $RE_{5-x}Mg_xGe_4$ were identified only as minor phases. Additionally, structure refinements for crystals obtained by this method showed no increased Mg content compared to crystals obtained via other routes. This is an indication that the compositions beyond the established range, although possible, are very difficult to achieve. This observation is discussed in the text within the context of the bonding and the formal electron count.

3. Metal flux reactions. These were intended to grow crystals of $RE_{5-x}Mg_xGe_4$ from an inert (under the present conditions) metal flux, such as Pb for example. Other low-melting metals, such as Al, Ga, In, and Sn were not pursued, since they are known to form a large number of compounds with germanium and the rare-earth metals. The reactions were carried out in alumina crucibles enclosed in fused silica tubes and flame-sealed under a vacuum. Various temperature profiles and nominal composition were tried, but suitable conditions for the growth of $RE_{5-x}Mg_xGe_4$ crystals were not found. The typical outcomes of the flux reaction were again *RE*-Ge binaries, as well as Mg_2Ge.

From the description above, it is apparent that much of the synthetic problems encountered in this system were due to the volatile Mg in the tubes. Often, there were noticeable differences in the products of otherwise similar reactions (in terms of loading stoichiometry and heat treatment) can be explained by the high volatility of Mg in the reaction vessels – a known and well-documented synthetic challenge even in mxed alkaline-earth-Mg systems. This problem has been previously noted in other Mg systems such as Gd_2MgGe_2, RE_2MgGe_2 (*RE* = Y, La-Nd, Sm, Gd, Tb), and $Sr_2Mg_{12}Ge_7$ compounds [Steinwand, S. J.; Hurng, W.-M.; Corbett, J. D. *J. Solid State Chem.* **1991**, *94*, 36]. Prolonged annealing at 973-1073 K, slow cooling, quenching to room temperature, slower or faster ramping rates did not result in improved yields. The best "recipe" for minimizing the negative effect of the low temperature of vaporization of Mg is to rotate the ampoules once the highest temperature was reached. This apparently allows for better mixing of Mg with the other components. Only such reactions produced phases where the refined compositions were very close to the expected and the amounts of side products were negligible.

Some specific points of relevance to each of the studied *RE*-Mg-Ge systems:

La-Mg-Ge. A reaction loaded according to the stoichiometry of La:Mg:Ge (3:2:4) and heated according to the 1523 K profile produced mixture of phases, one of which appears to be hitherto unknown - body-centered orthorhombic symmetry with unit cell parameters *a*=4.412(2) Å; *b*=7.510(3) Å; *c*=23.770(7) Å. Another reaction with the same stoichiometry treated differently led to the formation of La_2MgGe_2.

Ce-Mg-Ge. All reactions here, independent of the loading stoichiometry and temperature profile yielded Ce_2MgGe_2.

Pr-Mg-Ge. A reaction which was loaded according to the stoichiometry of Pr:Mg:Ge (3:2:4) and heated according to the 1523 K profile produced mixture of phases, one of which is the unknown compound mentioned in the La-Mg-Ge system: unit cell parameters *a*=4.38(1) Å; *b*=7.36(1) Å;

c=23.35(2) Å. Pr_2MgGe_2 was the main product of this reaction. Attempts to run the same reaction at lower temperature led to the formation of nearly phase-pure Pr_2MgGe_2.

Nd-Mg-Ge. A reaction which was loaded according to the stoichiometry of Nd:Mg:Ge (3:2:4) and heated according to the 1523 K profile produced Nd_2MgGe_2. Another reaction which was also loaded according to the same stoichiometry of Nd:Mg:Ge (3:2:4) but treated differently also led to the formation of Nd_2MgGe_2. A third reaction which was loaded according to the stoichiometry of Nd:Mg:Ge (4:1:4) and heated according to the 1323 K profile yielded Nd_5Ge_3 as a main product.

Sm-Mg-Ge. A reaction which was loaded according to the stoichiometry of Sm:Mg:Ge (4:1:4) and heated according to the heated according to the 1323 K profile produced Sm_5Ge_3. Another reaction done according to the same stoichiometry and reaction conditions except it was rotated at the highest temperature led to the formation of Sm_2MgGe_2. Using the same 4:1:4 stoichiometry but allowing the highest temperature to be achieved to be 1373 K for 20 h, led to the formation of Sm_5Ge_3.

All reactions which were loaded according to the stoichiometry of Sm:Mg:Ge (3:2:4) and heated according to the 1523 K profile led to the formation of Sm_2MgGe_2. The same was true for other "3:2:4" reactions done at lower temperatures (1373 K).

Eu-Mg-Ge. A reaction which was loaded according to the stoichiometry of Eu:Mg:Ge (4:1:4) and subjected to the 1373 K profile led to the formation of EuMgGe and EuGe. Another reaction with the 3:2:4 stoichiometry yielded $EuGe_2$ as a main product.

Gd-Mg-Ge. A reaction which was loaded according to the stoichiometry of Gd:Mg:Ge (4:1:4) and heated according to the 1373 K profile led to the formation of Gd_5Ge_3. The same product formed from a reaction, which was loaded according to the same stoichiometry and subjected to identical heating except that the tube was rotated at the highest temperature.

Reactions with the loading stoichiometry Gd:Mg:Ge (3:2:4) and subjected to the same reaction conditions as mentioned above, with or without rotation of the tube at the highest temperature afforded Gd_2MgGe_2.

A reaction loaded with the stoichiometry of Gd:Mg:Ge (4:1:4) and heated according to the 1523 K profile led to the formation of the desired phase. The same is true for a reaction loaded according to the stoichiometry of Gd:Mg:Ge (3:2:4) and heated according to the same temperature conditions.

Reactions which were done using an excess of Mg or using a Pb flux, and heated to 1273 K (rate 200°/h) produced GdGe, Gd_3Ge_4 and Mg_2Ge.

Tb-Mg-Ge. A reaction which was loaded according to the stoichiometry of Tb:Mg:Ge (4:1:4) and heated according to the 1373 K profile led to the formation of $Tb_{5-x}Mg_xGe_4$. An identical reaction, except not rotated at the highest temperature produced Tb_2MgGe_2. A reaction according to the same stoichiometry and subject to a lower temperature of 1323 K with rotation also led to the desired product. In all cases however, Tb_5Ge_3 was observed as a side product. The use of higher temperatures while using the same loading stoichiometry of Tb:Mg:Ge (4:1:4) seemed work as well, although no single-crystals could be found in order to refine the structure and the composition. A reaction loaded according to the stoichiometry of 3:2:4 and subjected to the 1523 K profile also produced the desired phase but with a substantial amount of Tb_2MgGe_2.

Reactions which were done using an excess of Mg or using Pb flux and heated to 1273 K produced predominantly $TbGe_{2-x}$, Tb_3Ge_4, Mg_2Ge and Tb_2MgGe_2. Several other reactions that were done by varying the amount of Mg while keeping the ratio of Tb:Ge to be 1:1 produced TbGe as a main product.

In a separate sets of experiments, the Tb:Ge ratio was varied while keeping the Mg:Ge ratio These reactions were also done at 1523 K. In all cases with Tb:Ge ratios of 2:1, 3:1, 4:1, these attempts led to formation of Tb_5Ge_3.

Dy-Mg-Ge. Similar to the Tb-system, a reaction which was loaded according to the stoichiometry of Dy:Mg:Ge (4:1:4) and heated according to the 1373 K profile led to the formation of $Dy_{5-x}Mg_xGe_4$. A similar reaction with the same stoichiometry and temperature profile except not rotated at the highest temperature produced Dy_2MgGe_2 alongside the desired product. Changing the loading stoichiometry to

Dy:Mg:Ge (4:3:4) while keeping the same conditions also led to the desired product. When Dy:Mg:Ge were loaded in the 3:2:4 ratio, and heated to 1373 K, Dy_2MgGe_2 was the product as well.

The use of higher temperatures while using reactions loaded according to the stoichiometry of Dy:Mg:Ge (4:1:4) seemed to go against the formation of the desired product. A reaction subjected to the 1523 K profile led to the formation of Dy_5Ge_3 and Dy_2MgGe_2. However, a reaction loaded according to the stoichiometry of 3:2:4 and subjected to the same heat treatment worked.

Reactions which were done using an excess of Mg or a Pb flux yielded DyGe, $DyGe_{2-x}$ and Mg_2Ge binaries.

Ho-Mg-Ge. Similar to the Tb- and Dy-systems, a reaction which was loaded according to the stoichiometry of Dy:Mg:Ge (4:1:4) and heated according to the 1373 K profile led to the formation of $Ho_{5-x}Mg_xGe_4$. A reaction which was done according to the same stoichiometry and heat treatment (without rotation) led to the formation of Ho_2MgGe_2. A reaction with the same stoichiometry but subject to a slightly lower temperature (1323 K) and rotated led to the formation of the desired product.

At higher temperatures (1523 K), when loading the reactions according to the stoichiometry of 4:1:4, $Ho_{5-x}Mg_xGe_4$ is synthesized almost phase-pure. For example, a reaction which was loaded according to the stoichiometry of Ho:Mg:Ge (3:2:4) produced $Ho_{3.05(1)}Mg_{1.95}Ge_4$. Lowering temperature to 1373 K for the same nominal composition favored the formation of Ho_2MgGe_2. Side products of such reactions were $Ho_{11-x}Mg_xGe_{10}$ ($Ho_{11}Ge_{10}$-type) along with Ho_3Ge_4.

Reaction which were done using an excess of Mg or Pb flux led to the formation of Ho_3Ge_4, HoGe, and Mg_2Ge.

Er-Mg-Ge. A reaction which was loaded according to the stoichiometry of Er:Mg:Ge (4:1:4) and heated according to the 1373 K profile and rotated at the highest temperature led to the formation of $Er_{5-x}Mg_xGe_4$. A reaction which was done according to the same stoichiometry and heated to the same temperatures except without rotation, did not produce the desired phase. A reaction which was loaded according to the stoichiometry of Er:Mg:Ge (3:2:4) and heated according to the 1373 K profile led to the

formation of Er_2MgGe_2. If a higher temperature was used, both for a reaction loaded with the stoichiometry of Er:Mg:Ge (4:1:4) or (3:2:4), $Er_{5-x}Mg_xGe_4$ was formed.

In further attempts to vary the heating profiles or initial loading stoichiometry, we had explored different compositional ranges and had come across three new structures for the heavier rare-earth elements of Er, Tm, and Lu. They exhibit substantial disorder and appear to be related to the $Ho_{11}Ge_{10}$ structure type, and will therefore be at the focus of a subsequent study.

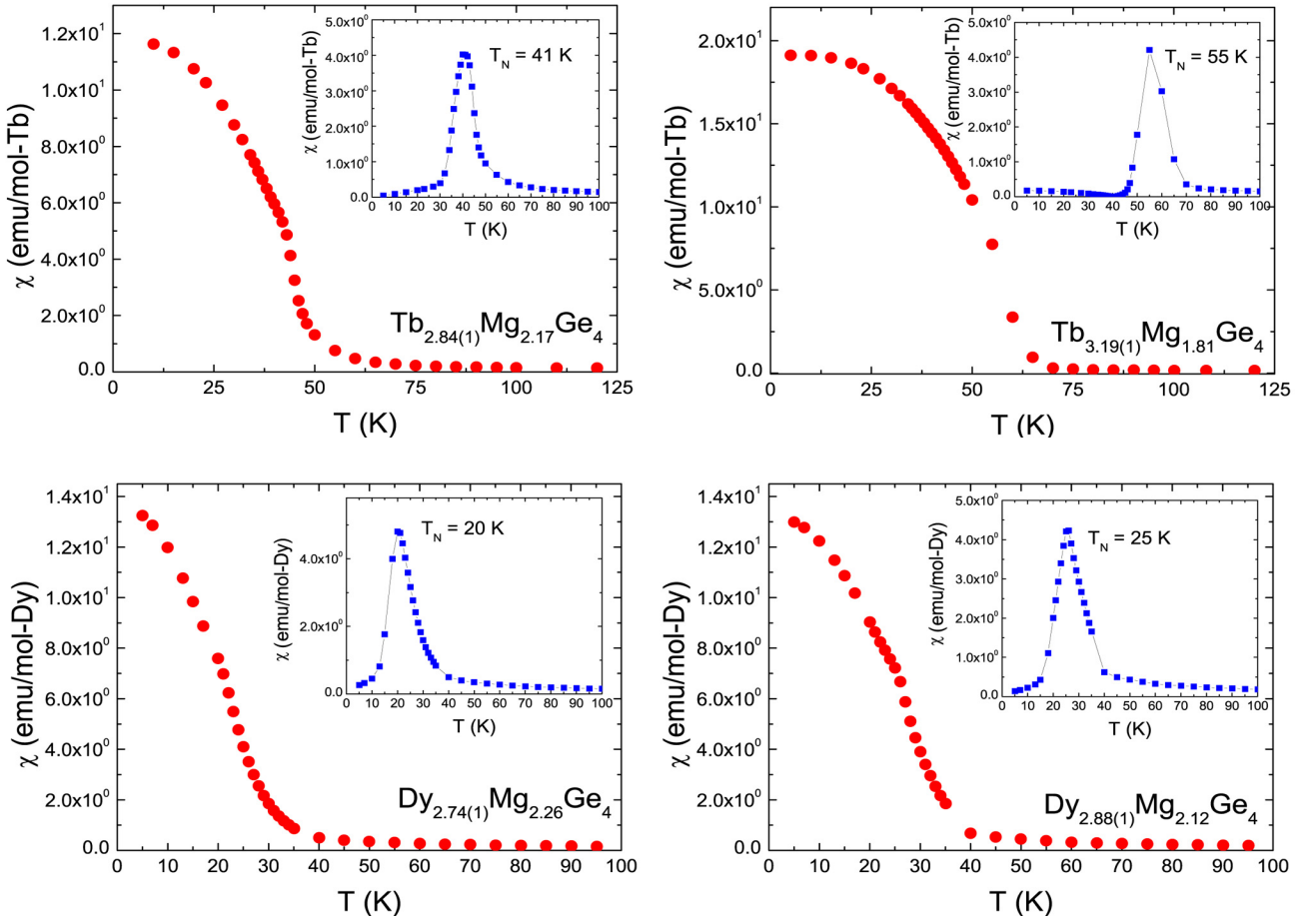
Tm-Mg-Ge. A reaction which was loaded according to the stoichiometry of Tm:Mg:Ge (4:1:4) and heated according to the 1373 K profile led to the formation of a $Tm_{11-x}Mg_xGe_{10}$ compound, in analogy with the Er-system. A reaction which was loaded according to the stoichiometry of Tm:Mg:Ge (3:2:4) and heated at the same temperature yielded Tm_2MgGe_2. If a higher temperature was used, both reactions loaded with the stoichiometry of Tm:Mg:Ge (4:1:4) and (3:2:4) led to the formation of $Tm_{5-x}Mg_xGe_4$.

Lu-Mg-Ge. A reaction which was loaded according to the stoichiometry of Lu:Mg:Ge (4:1:4) and heated according to the 1373 K profile led to the formation of a $Lu_{11-x}Mg_xGe_{10}$ compound, in analogy with the Er- and Tm-systems. For a reaction which was done according to the same stoichiometry and heated to the same temperatures except with rotation at the highest temperature, the product was $Lu_{5-x}Mg_XGe_4$. Reactions which were loaded according to the stoichiometry of Lu:Mg:Ge (3:2:4) and heated according to 1523 K produced Lu_2MgGe_2.

Y-Mg-Ge. A reaction which was loaded according to the stoichiometry of Y:Mg:Ge (4:1:4) and heated according to the 1373 K profile led to $Y_{5-x}Mg_xGe_4$. Using the same reaction conditions and stoichiometry except not rotating the reaction at the highest temperature also led to the desired product but with lower Mg content. A reaction done according to the loading stoichiometry of Y:Mg:Ge (3:2:4) and heated to 1523 K led to $Y_{5-x}Mg_xGe_4$. However using the 3:2:4 stoichiometry and only heating the reaction to 1373 K (rate 200°/h) and keeping it there for 20 h led to the formation of Y_2MgGe_2.

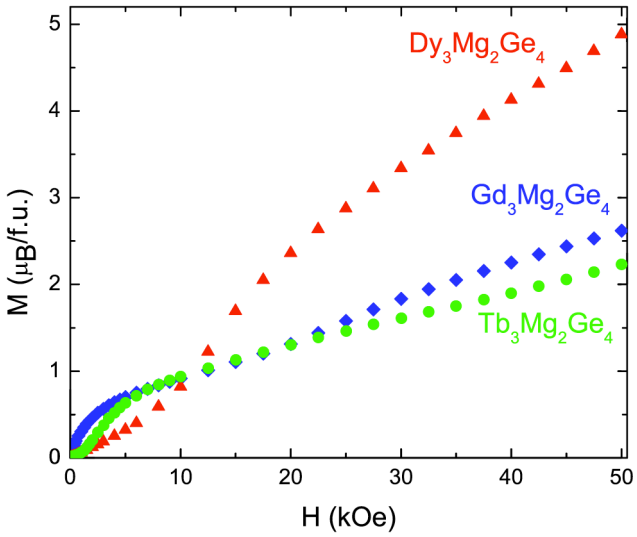
Additional magnetic susceptibility data

The magnetic susceptibility exhibited by the Tb- and Dy-samples is similar to that shown for the Ho-analogs discussed in the main text. Both show a difference in their respective ZFC and FC curves measured in a magnetic field of 100 Oe. Cusp-like features in the data attributed to the antiferromagnetic component of the magnetic structure can be seen at temperature ranging from ca. 55 K and 25 K respectively. Above these temperatures, the $\chi(T)$ data follow nicely a Curie-Weiss law and linear fits of the inverse susceptibility at the high temperature portion of the data results in effective magnetic moments in close agreement with the effective moments expected from the Hund's rule and positive Weiss temperatures (Table 5). It should be noted that the trend concerning the decrease in the ordering temperature in the $Ho_{5-x}Mg_xGe_4$ ($1.23 \leq x \leq 2.08$) samples with increased Mg content, is also observed for other Mg-richer compositions of the two compounds in agreement to that observed for $Tb_{5-x}Mg_xGe_4$ and $Dy_{5-x}Mg_xGe_4$ (see the plots below)



The χ(T) curves for $Er_{5-x}Mg_xGe_4$ and $Tm_{5-x}Mg_xGe_4$ do not show the signatures of magnetic order down to 5 K, the lowest measured temperature. This is can be expected since the ordering temperatures appear to follow the de Gennes factor $J(J+1)(g-1)^2$ of the specific lanthanide ion. The small hump around 50 K in the χ(T) data for $Tm_{3.51(1)}Mg_{1.49}Ge_4$ (Figure 4 in the main text) is almost certainly due to a impurity phase(s) present since it is not seen in the χ(T) data for $Tm_{5-x}Mg_xGe_4$ with different '*x*'. $Lu_{5-x}Mg_xGe_4$ and $Y_{5-x}Mg_xGe_4$ are Pauli-like paramagnetic and do not seem to enter in a superconducting state down to 5 K.

The *M* vs *H* curves for $Gd_{5-x}Mg_xGe_4$, $Tb_{5-x}Mg_xGe_4$ and $Dy_{5-x}Mg_xGe_4$ show no tendency for saturation in applied fields up to 50 kOe. As shown below, the plots look similar to that for $Ho_{5-x}Mg_xGe_4$ (Figure 5a). The maximum saturation moments per formula unit are ca. 2.5 μ_B, 2.0 μ_B, and 4.9 μ_B, for $Gd_{5-x}Mg_xGe_4$, $Tb_{5-x}Mg_xGe_4$ and $Dy_{5-x}Mg_xGe_4$, respectively.



These values are much lower than that expected *gJ* value of 7 μ_B for free-ion Gd^{3+}, 9 μ_B for free-ion Tb^{3+} and 10 μ_B for free-ion Dy^{3+}. There are steps in the isotherm, suggestive of spin-flip transitions, but they are not as clearly expressed as those for $Ho_{5-x}Mg_xGe_4$ (Figure 5a). This is likely due to the difference in T_C/T, which for $Gd_{5-x}Mg_xGe_4$, is ca. 110/5 while for $Ho_{5-x}Mg_xGe_4$, is ca. 20/5 (T = 5 K is the temperature at which the isotherms were obtained an T_C are the respective Curie temperatures – see Table 5 in the main text).

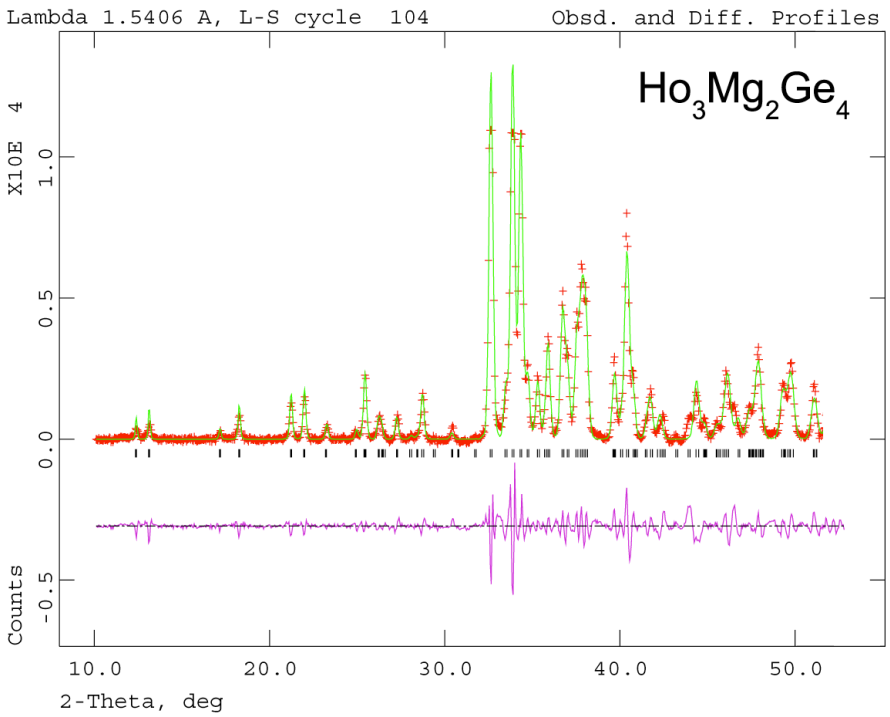


Figure S1. Room temperature powder pattern (Cu Kα) for $Ho_{3.05(1)}Mg_{1.95}Ge_4$. The calculated positions of the reflections are shown with black tick-marks. Experimental and calculated intensities are represented in red and green, respectively. The difference between them is shown in magenta.

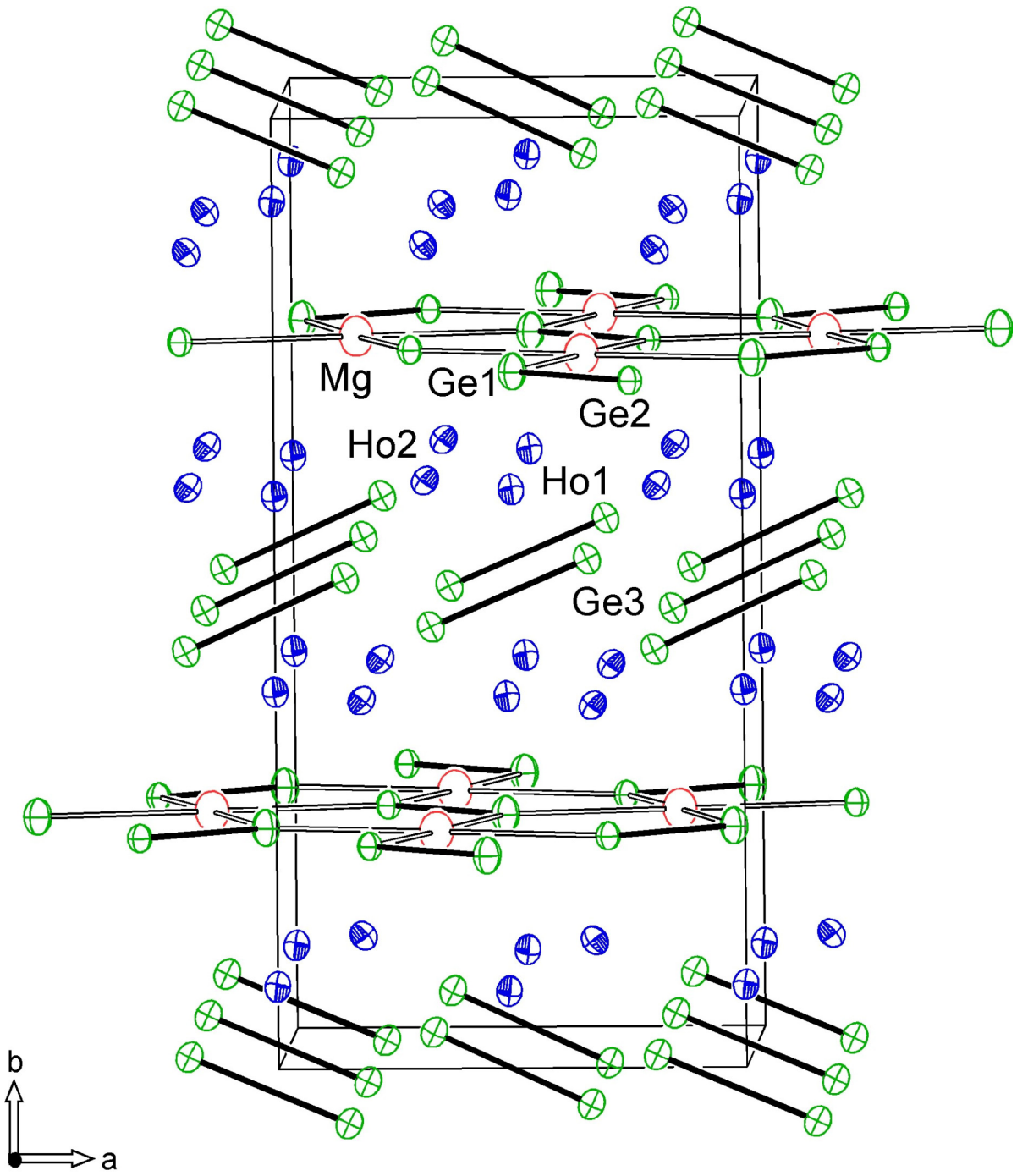


Figure S2. Representation of the refined structure of $Ho_{3.05(1)}Mg_{1.95}Ge_4$ with anisotropic displacement parameters. The thermal ellipsoids are drawn at the 95% probability level. Color code: *M*1 (mixed Ho/Mg) and *M*2 (Ho) – blue, full ellipsoids; Ge – green; crossed ellipsoids, Mg – red, open circles.

Table S1. Selected crystallographic data for Ho_5Ge_4 at 120 K.

empirical formula	Ho_5Ge_4
formula weight	1115.01
space group	*Pnma* (No. 62)
λ, Å	0.71073
T, K	120
a, Å	7.567(3)
b, Å	14.562(7)
c, Å	7.638(4)
V, Å^3, *Z* = 4	841.6(7)
c/*a*	1.009
ρ_{calcd}, g cm^{-3}	8.800
μ (Mo Kα), cm^{-1}	603.74
R_1 [I > 2σ(I)]	0.0369
wR_2 [I > 2σ(I)]	0.0570
R_1 [all data]	0.0662
wR_2 [all data]	0.0733

Table S2. Atomic coordinates and equivalent displacement parameters (U_{eq}) for Ho_5Ge_4.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Ho3	4*c*	0.28702(14)	1/4	0.00167(12)	0.0053(2)
Ho1	8*d*	0.12113(10)	0.11744(5)	0.33894(8)	0.0055(2)
Ho2	8*d*	-0.02842(10)	0.10034(5)	0.82328(9)	0.0059(2)
Ge1	4*c*	0.9175(3)	1/4	0.1157(3)	0.0064(5)
Ge2	4*c*	0.1673(3)	1/4	0.6377(3)	0.0061(5)
Ge3	8*d*	0.2193(2)	0.95604(11)	0.5322(2)	0.0064(4)

Table S3. Important distances (Å) in Ho_5Ge_4.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.707(3)	Ho3-	Ge1	2.928(3)
	Ho3	2.928(3)		Ge2	2.924(3)
	Ho1 (×2)	2.980(2)		Ge2	3.068(3)
	Ho1 (×2)	3.001(2)		Ge3 (×2)	3.0097(2)
	Ho2 (×2)	3.147(2)		Ge1	3.085(3)
Ge2-	Ge1	2.707(3)		Ho1 (×2)	3.406(2)
	Ho3	2.924(3)		Ho1 (×2)	3.455(2)
	Ho3	3.068(3)		Ho2 (×2)	3.5075(14)
	Ho2 (×2)	2.992(2)		Ho2 (×2)	3.5859(14)
	Ho1 (×2)	3.009(2)	Ho1-	Ho1 (×2)	4.020(2)
	Ho2 (×2)	3.184(2)		Ho1	3.861(2)
Ge3-	Ge3	3.591(2)		Ho2	3.476(2)
	Ho1	2.845(2)		Ho2	3.7081(15)
	Ho1	2.873(2)		Ho2	3.876(2)
	Ho1	2.958(2)		Ho2	4.106(2)
	Ho2	2.948(2)		Ho2	4.424(2)
	Ho3	3.0097(2)	Ho2-	Ho2 (×2)	3.946(2)
	Ho2	3.046(2)		Ho2	4.002(2)
	Ho2	3.183(2)		Ho1	3.476(2)
				Ho1	3.7081(15)
				Ho1	3.876(2)
				Ho1	4.106(2)
				Ho1	4.424(2)

Table S4. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Ho_{2.92(1)}Mg_{2.08}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3408(4)	1/4	-0.0104(3)	0.0089(5)
*M*1 [a]	8*d*	0.17007(6)	0.12618(3)	0.32188(5)	0.0051(2)
*M*2 [b]	8*d*	0.00606(3)	0.09512(2)	0.81671(3)	0.0054(1)
Ge1	4*c*	0.97234(11)	1/4	0.09868(11)	0.0074(2)
Ge2	4*c*	0.21288(11)	1/4	0.63789(10)	0.0049(2)
Ge3	8*d*	0.16877(8)	0.96298(4)	0.53428(7)	0.0053(1)

[a] Refined as a statistical mixture of Ho and Mg in a ratio 45.9:54.1
[b] Refined as 100% Ho

Table S5. Selected distances (Å) in $Ho_{2.92(1)}Mg_{2.08}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.5627(11)	Mg-	Ge1	2.711(3)
	Mg	2.711(3)		Ge2	2.780(3)
	*M*1 (×2)	2.8188(8)		Ge2	2.834(3)
	*M*1 (×2)	2.8220(8)		Ge3 (×2)	3.0580(8)
	*M*2 (×2)	3.0955(7)		Ge1	3.279(3)
Ge2-	Ge1	2.5627(11)		*M*1 (×2)	3.241(2)
	Mg	2.780(3)		*M*1 (×2)	3.316(2)
	Mg	2.834(3)		*M*2 (×2)	3.421(2)
	*M*2 (×2)	2.9741(6)		*M*2 (×2)	3.481(2)
	*M*1 (×2)	3.0073(8)	*M*1-	*M*1 (×2)	3.668(2)
	*M*2 (×2)	3.0351(7)		*M*1	3.5325(11)
Ge3-	Ge3	2.6403(12)		*M*2	3.5506(7)
	*M*1	2.7790(8)		*M*2	3.6450(6)
	*M*1	2.8382(8)		*M*2	3.886(2)
	*M*1	2.9069(8)		*M*2	3.977(2)
	*M*2	2.9381(7)		*M*2	4.053(2)
	Mg	3.0580(8)	*M*2-	*M*2 (×2)	3.946(2)
	*M*2	3.0630(7)		*M*2	4.359(2)
	*M*2	3.0838(7)		*M*1	3.5506(7)
				*M*1	3.6450(6)
				*M*1	3.886(2)
				*M*1	3.977(2)
				*M*1	4.053(2)

Table S6. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Ho_{3.20(1)}Mg_{1.80}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3416(7)	1/4	-0.0125(8)	0.0070(12)
*M*1 [a]	8*d*	0.17015(11)	0.12652(6)	0.32176(11)	0.0053(3)
*M*2 [b]	8*d*	0.00718(7)	0.09486(4)	0.81708(7)	0.0059(2)
Ge1	4*c*	0.9729(2)	1/4	0.0952(3)	0.0078(4)
Ge2	4*c*	0.2134(2)	1/4	0.6385(2)	0.0056(4)
Ge3	8*d*	0.1684(2)	0.96320(9)	0.5340(2)	0.0062(3)

[a] Refined as a statistical mixture of Ho and Mg in a ratio 59.8:40.2
[b] Refined as 100% Ho

Table S7. Selected distances (Å) in $Ho_{3.20(1)}Mg_{1.80}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.555(3)	Mg-	Ge1	2.719(6)
	Mg	2.719(6)		Ge2	2.784(6)
	*M*1 (×2)	2.838(2)		Ge2	2.822(6)
	*M*1 (×2)	2.839(2)		Ge3 (×2)	3.073(2)
	*M*2 (×2)	3.087(2)		Ge1	3.327(5)
Ge2-	Ge1	2.555(4)		*M*1 (×2)	3.254(5)
	Mg	2.784(6)		*M*1 (×2)	3.337(5)
	Mg	2.822(6)		*M*2 (×2)	3.425(5)
	*M*2 (×2)	2.9837(13)		*M*2 (×2)	3.487(4)
	*M*1 (×2)	3.017(2)	*M*1-	*M*1 (×2)	3.681(2)
	*M*2 (×2)	3.0512(13)		*M*1	3.535(2)
Ge3-	Ge3	2.642(3)		*M*2	3.5674(11)
	*M*1	2.792(2)		*M*2	3.6699(11)
	*M*1	2.848(2)		*M*2	3.897(2)
	*M*1	2.921(2)		*M*2	3.989(2)
	*M*2	2.9406(14)		*M*2	4.058(2)
	Mg	3.0731(13)	*M*2-	*M*2 (×2)	3.6602(7)
	*M*2	3.0734(16)		*M*2	3.904(2)
	*M*2	3.0886(14)		*M*1	3.5674(11)
				*M*1	3.6699(11)
				*M*1	3.897(2)
				*M*1	3.989(2)
				*M*1	4.058(2)

Table S8. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Ho_{3.29(1)}Mg_{1.71}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3409(4)	1/4	-0.0137(4)	0.0082(6)
*M*1 [a]	8*d*	0.17009(5)	0.12650(3)	0.32192(5)	0.0052(2)
*M*2 [b]	8*d*	0.00763(4)	0.09463(2)	0.81714(3)	0.00570(10)
Ge1	4*c*	0.97419(12)	1/4	0.09437(12)	0.0074(2)
Ge2	4*c*	0.21367(12)	1/4	0.63832(11)	0.0052(2)
Ge3	8*d*	0.16849(9)	0.96320(4)	0.53365(8)	0.0059(2)

[a] Refined as a statistical mixture of Ho and Mg in a ratio 64.4:35.6
[b] Refined as 100% Ho

Table S9. Selected distances (Å) in $Ho_{3.29(1)}Mg_{1.71}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.556(2)	Mg-	Ge1	2.709(3)
	Mg	2.709(3)		Ge2	2.790(3)
	*M*1 (×2)	2.8412(13)		Ge2	2.812(3)
	*M*1 (×2)	2.8496(14)		Ge3 (×2)	3.0792(8)
	*M*2 (×2)	3.087(2)		Ge1	3.346(4)
Ge2-	Ge1	2.556(2)		*M*1 (×2)	3.264(3)
	Mg	2.790(3)		*M*1 (×2)	3.345(3)
	Mg	2.812(3)		*M*2 (×2)	3.427(3)
	*M*2 (×2)	2.9898(13)		*M*2 (×2)	3.484(3)
	*M*1 (×2)	3.018(2)	*M*1-	*M*1 (×2)	3.685(2)
	*M*2 (×2)	3.0582(14)		*M*1	3.541(2)
Ge3-	Ge3	2.645(2)		*M*2	3.571(2)
	*M*1	2.7965(14)		*M*2	3.673(2)
	*M*1	2.848(2)		*M*2	3.897(2)
	*M*1	2.9237(14)		*M*2	3.988(2)
	*M*2	2.9372(14)		*M*2	4.058(2)
	Mg	3.073(2)	*M*2-	*M*2 (×2)	3.664(2)
	*M*2	3.079(2)		*M*2	3.902(2)
	*M*2	3.0899(13)		*M*1	3.571(2)
				*M*1	3.673(2)
				*M*1	3.897(2)
				*M*1	3.988(2)
				*M*1	4.058(2)

Table S10. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Ho_{3.62(1)}Mg_{1.38}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3406(7)	1/4	-0.0162(7)	0.0102(11)
*M*1 [a]	8*d*	0.16920(8)	0.12675(4)	0.32197(8)	0.0057(2)
*M*2 [b]	8*d*	0.00814(7)	0.09428(3)	0.81764(6)	0.0061(1)
Ge1	4*c*	0.9750(2)	1/4	0.0912(2)	0.0078(4)
Ge2	4*c*	0.2131(2)	1/4	0.6386(2)	0.0063(3)
Ge3	8*d*	0.1695(2)	0.96359(8)	0.5339(2)	0.0066(3)

[a] Refined as a statistical mixture of Ho and Mg in a ratio 80.7:19.3
[b] Refined as 100% Ho

Table S11. Selected distances (Å) in $Ho_{3.62(1)}Mg_{1.38}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.556(2)	Mg-	Ge1	2.714(5)
	Mg	2.714(5)		Ge2	2.794(6)
	*M*1 (×2)	2.8584(14)		Ge2	2.795(5)
	*M*1 (×2)	2.8767(14)		Ge3 (×2)	3.1043(14)
	*M*2 (×2)	3.0807(12)		Ge1	3.392(4)
Ge2-	Ge1	2.556(2)		*M*1 (×2)	3.282(5)
	Mg	2.794(6)		*M*1 (×2)	3.368(5)
	Mg	2.795(5)		*M*2 (×2)	3.432(4)
	*M*2 (×2)	3.0036(12)		*M*2 (×2)	3.491(4)
	*M*1 (×2)	3.0237(14)	*M*1-	*M*1 (×2)	3.704(2)
	*M*2 (×2)	3.0833(12)		*M*1	3.5542(13)
Ge3-	Ge3	2.668(2)		*M*2	3.5880(9)
	*M*1	2.8056(13)		*M*2	3.6864(9)
	*M*1	2.8585(13)		*M*2	3.920(2)
	*M*1	2.9413(14)		*M*2	3.993(2)
	*M*2	2.9392(13)		*M*2	4.056(2)
	Mg	3.1043(14)	*M*2-	*M*2 (×2)	3.6843(6)
	*M*2	3.0869(13)		*M*2	3.901(2)
	*M*2	3.0952(13)		*M*1	3.5880(9)
				*M*1	3.6864(9)
				*M*1	3.920(2)
				*M*1	3.993(2)
				*M*1	4.056(2)

Table S12. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Ho_{3.77(1)}Mg_{1.23}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3393(7)	1/4	-0.0178(7)	0.0071(11)
*M*1 [a]	8*d*	0.16927(8)	0.12684(4)	0.32215(7)	0.0045(2)
*M*2 [b]	8*d*	0.00869(7)	0.09413(4)	0.81778(6)	0.0049(2)
Ge1	4*c*	0.9752(2)	1/4	0.0897(2)	0.0056(4)
Ge2	4*c*	0.2128(2)	1/4	0.6381(2)	0.0045(4)
Ge3	8*d*	0.1699(2)	0.96383(8)	0.53364(14)	0.0053(3)

[a] Refined as a statistical mixture of Ho and Mg in a ratio 88.6:11.4
[b] Refined as 100% Ho

Table S13. Selected distances (Å) in $Ho_{3.77(1)}Mg_{1.23}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.551(2)	Mg-	Ge1	2.708(6)
	Mg	2.708(6)		Ge2	2.786(6)
	*M*1 (×2)	2.8691(14)		Ge2	2.802(6)
	*M*1 (×2)	2.8841(14)		Ge3 (×2)	3.115(2)
	*M*2 (×2)	3.0780(13)		Ge1	3.421(2)
Ge2-	Ge1	2.551(2)		*M*1 (×2)	3.299(5)
	Mg	2.786(6)		*M*1 (×2)	3.378(4)
	Mg	2.802(6)		*M*2 (×2)	3.435(4)
	*M*2 (×2)	3.0096(12)		*M*2 (×2)	3.485(4)
	*M*1 (×2)	3.0216(14)	*M*1-	*M*1 (×2)	3.711(2)
	*M*2 (×2)	3.0948(12)		*M*1	3.5581(13)
Ge3-	Ge3	2.674(2)		*M*2	3.5957(9)
	*M*1	2.8121(13)		*M*2	3.6917(9)
	*M*1	2.8590(13)		*M*2	3.924(2)
	*M*1	2.9515(14)		*M*2	3.995(2)
	*M*2	2.9370(13)		*M*2	4.059(2)
	Mg	3.115(2)	*M*2-	*M*2 (×2)	3.6916(7)
	*M*2	3.0923(13)		*M*2	3.901(2)
	*M*2	3.0973(13)		*M*1	3.5957(9)
				*M*1	3.6917(9)
				*M*1	3.924(2)
				*M*1	3.995(2)
				*M*1	4.059(2)

Table S14. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Gd_{3.55(1)}Mg_{1.45}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3423(6)	1/4	-0.0196(6)	0.0102(11)
*M*1 [a]	8*d*	0.17091(8)	0.12696(5)	0.32082(7)	0.0059(2)
*M*2 [b]	8*d*	0.01002(6)	0.09496(4)	0.81732(6)	0.0065(2)
Ge1	4*c*	0.9760(2)	1/4	0.0892(2)	0.0092(3)
Ge2	4*c*	0.21556(2)	1/4	0.6368(2)	0.0064(3)
Ge3	8*d*	0.16560(14)	0.96371(8)	0.53326(13)	0.0070(3)

[a] Refined as a statistical mixture of Gd and Mg in a ratio 77.2:22.8
[b] Refined as 100% Gd

Table S15. Selected distances (Å) in $Gd_{3.55(1)}Mg_{1.45}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.570(3)	Mg-	Ge1	2.757(6)
	Mg	2.757(6)		Ge2	2.830(6)
	*M*1 (×2)	2.913(2)		Ge2	2.837(6)
	*M*1 (×2)	2.928(2)		Ge3 (×2)	3.178(2)
	*M*2 (×2)	3.116(2)		Ge1	3.492(2)
Ge2-	Ge1	2.570(3)		*M*1 (×2)	3.355(5)
	Mg	2.830(6)		*M*1 (×2)	3.437(5)
	Mg	2.837(6)		*M*2 (×2)	3.468(5)
	*M*2 (×2)	3.0555(14)		*M*2 (×2)	3.529(5)
	*M*1 (×2)	3.064(2)	*M*1-	*M*1 (×2)	3.745(2)
	*M*2 (×2)	3.1304(14)		*M*1	3.5982(14)
Ge3-	Ge3	2.704(3)		*M*2	3.6554(9)
	*M*1	2.858(2)		*M*2	3.7445(5)
	*M*1	2.913(2)		*M*2	3.968(2)
	*M*1	2.997(2)		*M*2	4.058(2)
	*M*2	2.998(2)		*M*2	4.110(2)
	Mg	3.178(2)	*M*2-	*M*2 (×2)	3.7288(5)
	*M*2	3.145(2)		*M*2	3.977(2)
	*M*2	3.1508(14)		*M*1	3.6554(9)
				*M*1	3.7445(5)
				*M*1	3.968(2)
				*M*1	4.058(2)
				*M*1	4.110(2)

Table S16. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Tb_{3.52(1)}Mg_{1.48}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3413(6)	1/4	-0.0173(5)	0.0086(8)
*M*1 [a]	8*d*	0.17046(7)	0.12685(3)	0.32131(6)	0.0059(2)
*M*2 [b]	8*d*	0.00982(6)	0.09487(3)	0.81736(5)	0.0066(2)
Ge1	4*c*	0.9758(2)	1/4	0.0907(2)	0.0089(3)
Ge2	4*c*	0.2153(2)	1/4	0.6372(2)	0.0069(3)
Ge3	8*d*	0.16651(13)	0.96368(6)	0.53345(11)	0.0072(2)

[a] Refined as a statistical mixture of Tb and Mg in a ratio 76.1:23.9
[b] Refined as 100% Tb

Table S17. Selected distances (Å) in $Tb_{3.52(1)}Mg_{1.48}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.559(2)	Mg-	Ge1	2.736(5)
	Mg	2.736(5)		Ge2	2.819(5)
	*M*1 (×2)	2.881(2)		Ge2	2.823(5)
	*M*1 (×2)	2.897(2)		Ge3 (×2)	3.126(3)
	*M*2 (×2)	3.097(2)		Ge1	3.435(2)
Ge2-	Ge1	2.559(2)		*M*1 (×2)	3.316(4)
	Mg	2.819(5)		*M*1 (×2)	3.396(4)
	Mg	2.823(5)		*M*2 (×2)	3.449(4)
	*M*2 (×2)	3.026(2)		*M*2 (×2)	3.505(3)
	*M*1 (×2)	3.043(2)	*M*1-	*M*1 (×2)	3.731(2)
	*M*2 (×2)	3.098(2)		*M*1	3.574(3)
Ge3-	Ge3	2.649(2)		*M*2	3.627(2)
	*M*1	2.834(2)		*M*2	3.725(2)
	*M*1	2.881(2)		*M*2	3.943(2)
	*M*1	2.959(2)		*M*2	4.030(2)
	*M*2	2.973(2)		*M*2	4.088(2)
	Mg	3.126(3)	*M*2-	*M*2 (×2)	3.713(2)
	*M*2	3.108(2)		*M*2	3.947(2)
	*M*2	3.113(2)		*M*1	3.627(2)
				*M*1	3.725(2)
				*M*1	3.943(2)
				*M*1	4.030(2)
				*M*1	4.088(2)

Table S18. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Dy_{3.50(1)}Mg_{1.50}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3417(8)	1/4	-0.0162(8)	0.0082(13)
*M*1 [a]	8*d*	0.17058(10)	0.12685(5)	0.32175(10)	0.0059(2)
*M*2 [b]	8*d*	0.00899(8)	0.09462(4)	0.81735(8)	0.0063(2)
Ge1	4*c*	0.9749(3)	1/4	0.0911(3)	0.0078(4)
Ge2	4*c*	0.2145(3)	1/4	0.6377(3)	0.0063(4)
Ge3	8*d*	0.1677(2)	0.96352(9)	0.5337(2)	0.0069(3)

[a] Refined as a statistical mixture of Dy and Mg in a ratio 74.9:25.1
[b] Refined as 100% Dy

Table S19. Selected distances (Å) in $Dy_{3.50(1)}Mg_{1.50}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.549(3)	Mg-	Ge1	2.726(6)
	Mg	2.726(6)		Ge2	2.802(6)
	*M*1 (×2)	2.867(2)		Ge2	2.809(7)
	*M*1 (×2)	2.873(2)		Ge3 (×2)	3.105(2)
	*M*2 (×2)	3.084(2)		Ge1	3.401(2)
Ge2-	Ge1	2.549(3)		*M*1 (×2)	3.289(5)
	Mg	2.802(6)		*M*1 (×2)	3.372(6)
	Mg	2.809(7)		*M*2 (×2)	3.434(5)
	*M*2 (×2)	3.0084(14)		*M*2 (×2)	3.495(5)
	*M*1 (×2)	3.025(2)	*M*1-	*M*1 (×2)	3.710(2)
	*M*2 (×2)	3.0815(14)		*M*1	3.553(2)
Ge3-	Ge3	2.650(3)		*M*2	3.6012(11)
	*M*1	2.813(2)		*M*2	3.6961(11)
	*M*1	2.865(2)		*M*2	3.919(2)
	*M*1	2.946(2)		*M*2	4.005(2)
	*M*2	2.952(2)		*M*2	4.070(2)
	Mg	3.105(2)	*M*2-	*M*2 (×2)	3.6905(8)
	*M*2	3.091(2)		*M*2	3.918(2)
	*M*2	3.098(2)		*M*1	3.6012(11)
				*M*1	3.6961(11)
				*M*1	3.919(2)
				*M*1	4.005(2)
				*M*1	4.070(2)

Table S20. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Er_{3.41(1)}Mg_{1.59}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3400(4)	1/4	-0.0140(4)	0.0076(6)
*M*1 [a]	8*d*	0.16938(5)	0.12650(3)	0.32245(5)	0.0051(1)
*M*2 [b]	8*d*	0.00717(4)	0.09425(2)	0.81735(4)	0.0058(1)
Ge1	4*c*	0.97381(14)	1/4	0.09388(13)	0.0072(2)
Ge2	4*c*	0.21254(13)	1/4	0.63902(12)	0.0054(2)
Ge3	8*d*	0.16971(10)	0.96344(5)	0.53389(9)	0.0060(2)

[a] Refined as a statistical mixture of Er and Mg in a ratio 70.4:29.6
[b] Refined as 100% Er

Table S21. Selected distances (Å) in $Er_{3.41(1)}Mg_{1.59}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.5548(14)	Mg-	Ge1	2.700(3)
	Mg	2.700(3)		Ge2	2.785(3)
	*M*1 (×2)	2.8377(8)		Ge2	2.796(3)
	*M*1 (×2)	2.8459(9)		Ge3 (×2)	3.0761(8)
	*M*2 (×2)	3.0785(8)		Ge1	3.342(2)
Ge2-	Ge1	2.5548(14)		*M*1 (×2)	3.257(3)
	Mg	2.785(3)		*M*1 (×2)	3.340(3)
	Mg	2.796(3)		*M*2 (×2)	3.422(2)
	*M*2 (×2)	2.9829(7)		*M*2 (×2)	3.476(2)
	*M*1 (×2)	3.0092(9)	*M*1-	*M*1 (×2)	3.681(2)
	*M*2 (×2)	3.0586(7)		*M*1	3.536(8)
Ge3-	Ge3	2.6536(14)		*M*2	3.5567(5)
	*M*1	2.7904(8)		*M*2	3.6608(5)
	*M*1	2.8369(8)		*M*2	3.890(2)
	*M*1	2.9201(8)		*M*2	3.973(2)
	*M*2	2.9260(7)		*M*2	4.047(2)
	Mg	3.0761(8)	*M*2-	*M*2 (×2)	3.6582(3)
	*M*2	3.0684(7)		*M*2	3.881(2)
	*M*2	3.0804(7)		*M*1	3.5567(5)
				*M*1	3.6608(5)
				*M*1	3.890(2)
				*M*1	3.973(2)
				*M*1	4.047(2)

Table S22. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Tm_{3.51(1)}Mg_{1.49}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3381(6)	1/4	-0.0136(6)	0.0050(9)
*M*1 [a]	8*d*	0.16878(7)	0.12641(4)	0.32283(7)	0.0039(2)
*M*2 [b]	8*d*	0.00696(6)	0.09386(3)	0.81769(6)	0.00444(14)
Ge1	4*c*	0.9740(2)	1/4	0.0933(2)	0.0059(3)
Ge2	4*c*	0.2121(2)	1/4	0.6394(2)	0.0045(3)
Ge3	8*d*	0.1708(2)	0.96342(7)	0.53407(14)	0.0052(2)

[a] Refined as a statistical mixture of Tm and Mg in a ratio 75.6:24.4
[b] Refined as 100% Tm

Table S23. Selected distances (Å) in $Tm_{3.51(1)}Mg_{1.49}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.550(2)	Mg-	Ge1	2.680(5)
	Mg	2.680(5)		Ge2	2.781(5)
	*M*1 (×2)	2.8316(13)		Ge2	2.791(5)
	*M*1 (×2)	2.8455(13)		Ge3 (×2)	3.0677(12)
	*M*2 (×2)	3.0670(12)		Ge1	3.333(2)
Ge2-	Ge1	2.550(2)		*M*1 (×2)	3.254(4)
	Mg	2.781(5)		*M*1 (×2)	3.326(4)
	Mg	2.791(5)		*M*2 (×2)	3.421(4)
	*M*2 (×2)	2.9782(10)		*M*2 (×2)	3.464(4)
	*M*1 (×2)	2.9982(13)	*M*1-	*M*1 (×2)	3.677(2)
	*M*2 (×2)	3.0575(11)		*M*1	3.5273(11)
Ge3-	Ge3	2.664(2)		*M*2	3.5412(7)
	*M*1	2.7795(12)		*M*2	3.6474(8)
	*M*1	2.8261(12)		*M*2	3.880(2)
	*M*1	2.9149(12)		*M*2	3.956(2)
	*M*2	2.9119(11)		*M*2	4.030(2)
	Mg	3.0677(12)	*M*2-	*M*2 (×2)	3.6478(8)
	*M*2	3.0608(11)		*M*2	3.855(2)
	*M*2	3.0709(11)		*M*1	3.5412(7)
				*M*1	3.6474(8)
				*M*1	3.880(2)
				*M*1	3.956(2)
				*M*1	4.030(2)

Table S24. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Lu_{3.60(1)}Mg_{1.40}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3375(6)	1/4	-0.0137(6)	0.0067(8)
*M*1 [a]	8*d*	0.16695(6)	0.12637(3)	0.32326(6)	0.0050(2)
*M*2 [b]	8*d*	0.00504(5)	0.09322(2)	0.81787(5)	0.0055(1)
Ge1	4*c*	0.9723(2)	1/4	0.0935(2)	0.0064(3)
Ge2	4*c*	0.2087(2)	1/4	0.6406(2)	0.0046(3)
Ge3	8*d*	0.17355(13)	0.96346(6)	0.53456(12)	0.0059(2)

[a] Refined as a statistical mixture of Lu and Mg in a ratio 80.1:19.9
[b] Refined as 100% Lu

Table S25. Selected distances (Å) in $Lu_{3.60(1)}Mg_{1.40}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.552(2)	Mg-	Ge1	2.674(4)
	Mg	2.674(4)		Ge2	2.761(4)
	*M*1 (×2)	2.8204(11)		Ge2	2.765(4)
	*M*1 (×2)	2.8326(11)		Ge3 (×2)	3.0591(11)
	*M*2 (×2)	3.0611(10)		Ge1	3.314(5)
Ge2-	Ge1	2.552(2)		*M*1 (×2)	3.232(3)
	Mg	2.761(4)		*M*1 (×2)	3.317(4)
	Mg	2.764(4)		*M*2 (×2)	3.410(3)
	*M*2 (×2)	2.9645(9)		*M*2 (×2)	3.460(3)
	*M*1 (×2)	2.9890(11)	*M*1-	*M*1 (×2)	3.659(2)
	*M*2 (×2)	3.0570(9)		*M*1	3.5172(9)
Ge3-	Ge3	2.686(2)		*M*2	3.5119(6)
	*M*1	2.7633(10)		*M*2	3.6260(6)
	*M*1	2.8151(10)		*M*2	3.872(2)
	*M*1	2.9033(10)		*M*2	3.935(2)
	*M*2	2.8915(10)		*M*2	4.013(2)
	Mg	3.0591(11)	*M*2-	*M*2 (×2)	3.635(2)
	*M*2	3.0502(10)		*M*2	3.824(2)
	*M*2	3.0623(10)		*M*1	3.5119(6)
				*M*1	3.6260(6)
				*M*1	3.872(2)
				*M*1	3.935(2)
				*M*1	4.013(2)

Table S26. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Y_{3.49(1)}Mg_{1.51}Ge_4$.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3409(9)	1/4	-0.0160(7)	0.0112(13)
*M*1 [a]	8*d*	0.1707(2)	0.12642(11)	0.3220(2)	0.0098(5)
*M*2 [b]	8*d*	0.0085(2)	0.09488(8)	0.81736(14)	0.0104(3)
Ge1	4*c*	0.9748(3)	1/4	0.0928(2)	0.0116(4)
Ge2	4*c*	0.2138(3)	1/4	0.6377(2)	0.0090(4)
Ge3	8*d*	0.1676(2)	0.96333(9)	0.5337(2)	0.0102(3)

[a] Refined as a statistical mixture of Y and Mg in a ratio 74.6:25.4
[b] Refined as 100% Y

Table S27. Selected distances (Å) in $Y_{3.49(1)}Mg_{1.51}Ge_4$.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.5587(14)	Mg-	Ge1	2.713(3)
	Mg	2.713(3)		Ge2	2.779(3)
	*M*1 (×2)	2.8265(9)		Ge2	2.826(3)
	*M*1 (×2)	2.8295(9)		Ge3 (×2)	3.0635(8)
	*M*2 (×2)	3.0900(8)		Ge1	3.302(3)
Ge2-	Ge1	2.5587(14)		*M*1 (×2)	3.246(3)
	Mg	2.779(3)		*M*1 (×2)	3.327(3)
	Mg	2.826(3)		*M*2 (×2)	3.420(3)
	*M*2 (×2)	2.9773(7)		*M*2 (×2)	3.481(3)
	*M*1 (×2)	3.0092(9)	*M*1-	*M*1 (×2)	3.713(2)
	*M*2 (×2)	3.0421(7)		*M*1	3.575(3)
Ge3-	Ge3	2.6411(14)		*M*2	3.607(2)
	*M*1	2.7843(9)		*M*2	3.699(2)
	*M*1	2.8387(9)		*M*2	3.926(2)
	*M*1	2.9116(9)		*M*2	4.018(2)
	*M*2	2.9362(8)		*M*2	4.086(20
	Mg	3.0635(8)	*M*2-	*M*2 (×2)	3.6918(11)
	*M*2	3.0669(8)		*M*2	3.937(2)
	*M*2	3.0842(8)		*M*1	3.607(2)
				*M*1	3.699(2)
				*M*1	3.926(2)
				*M*1	4.018(2)
				*M*1	4.086(2)

Table S28. Table S28. Selected crystallographic information for $Ho_{3.05(1)}Mg_{1.95}Ge_4$ at 298 K.

empirical formula	$Ho_{3.05(1)}Mg_{1.95}Ge_4$
formula weight	840.80
space group	*Pnma* (No. 62)
λ, Å	0.71073
T, K	298
a, Å	7.0226(7)
b, Å	14.3200(14)
c, Å	7.6636(8)
V, Å^3, $Z = 4$	770.68(13)
c/*a*	1.091
ρ_{calcd}, g cm^{-3}	7.254
μ (Mo Kα), cm^{-1}	464.08
R_1 [$I > 2\sigma(I)$]	0.0231
wR_2 [$I > 2\sigma(I)$]	0.0309
R_1 [all data]	0.0472
wR_2 [all data]	0.0495

Table S29. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Ho_{3.05(1)}Mg_{1.95}Ge_4$ at 298 K.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3409(4)	1/4	-0.0113(4)	0.0136(7)
*M*1 [a]	8*d*	0.16973(7)	0.12622(4)	0.32212(7)	0.0101(2)
*M*2 [b]	8*d*	0.00634(4)	0.09497(2)	0.81689(4)	0.01048(11)
Ge1	4*c*	0.97254(14)	1/4	0.09727(14)	0.0127(2)
Ge2	4*c*	0.21274(13)	1/4	0.63804(13)	0.0102(2)
Ge3	8*d*	0.16924(10)	0.96315(5)	0.53416(9)	0.0108(2)

[a] Refined as a statistical mixture of Ho and Mg in a ratio 52.6:47.4
[b] Refined as 100% Ho

Table S30. Selected distances (Å) in $Ho_{3.05(1)}Mg_{1.95}Ge_4$ at 298 K.

Atom pair		Distance (Å)	Atom pair		Distance (Å)
Ge1-	Ge2	2.5653(14)	Mg-	Ge1	2.718(3)
	Mg	2.718(3)		Ge2	2.786(3)
	*M*1 (×2)	2.8335(9)		Ge2	2.834(3)
	*M*1 (×2)	2.8364(9)		Ge3 (×2)	3.0730(8)
	*M*2 (×2)	3.0987(9)		Ge1	3.305(4)
Ge2-	Ge1	2.5653(14)		*M*1 (×2)	3.252(3)
	Mg	2.786(3)		*M*1 (×2)	3.316(2)
	Mg	2.834(3)		*M*2 (×2)	3.334(3)
	*M*2 (×2)	2.9847(7)		*M*2 (×2)	3.430(2)
	*M*1 (×2)	3.0157(10)	*M*1-	*M*1 (×2)	3.681(2)
	*M*2 (×2)	3.0494(7)		*M*1	3.5449(11)
Ge3-	Ge3	2.6529(14)		*M*2	3.5632(7)
	*M*1	2.7905(9)		*M*2	3.6663(6)
	*M*1	2.8449(9)		*M*2	3.900(2)
	*M*1	2.9186(9)		*M*2	3.987(2)
	*M*2	2.9420(8)		*M*2	4.063(2)
	Mg	3.0730(8)	*M*2-	*M*2 (×2)	3.6579(4)
	*M*2	3.0742(8)		*M*2	3.909(2)
	*M*2	3.0930(8)		*M*1	3.5632(7)
				*M*1	3.6663(6)
				*M*1	3.900(2)
				*M*1	3.987(2)
				*M*1	4.063(2)

Table S31. Selected crystallographic information for $Gd_{3.55(1)}Mg_{1.45}Ge_4$ at 298 K and 90 K.

empirical formula	$Gd_{3.55(1)}Mg_{1.45}Ge_4$	
formula weight	883.51	
space group	*Pnma* (No. 62)	
λ, Å	0.71073	
T, K	298	90
a, Å	7.1767(9)	7.1522(11)
b, Å	14.677(2)	14.613(2)
c, Å	7.7930(9)	7.7775(12)
V, Å^3, *Z* = 4	820.9(2)	812.8(2)
c/*a*	1.086	1.087
ρ_{calcd}, g cm^{-3}	7.152	7.222
μ (Mo Kα), cm^{-1}	429.01	430.53
R_1 [I > 2σ(I)]	0.0317	0.0337
wR_2 [I > 2σ(I)]	0.0535	0.0525
R_1 [all data]	0.0568	0.0616
wR_2 [all data]	0.0620	0.0669

Table S32. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Gd_{3.55(1)}Mg_{1.45}Ge_4$ at 298 K.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3404(7)	1/4	-0.0189(6)	0.0148(11)
*M*1 [a]	8*d*	0.17078(9)	0.12693(4)	0.32104(7)	0.0094(2)
*M*2 [b]	8*d*	0.01009(7)	0.09510(3)	0.81734(6)	0.0108(2)
Ge1	4*c*	0.9765(2)	1/4	0.0889(2)	0.0131(4)
Ge2	4*c*	0.2154(2)	1/4	0.6365(2)	0.0111(4)
Ge3	8*d*	0.1662(2)	0.96402(7)	0.53353(14)	0.0118(3)

Table S33. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Gd_{3.55(1)}Mg_{1.45}Ge_4$ at 90 K.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3416(7)	1/4	-0.0197(6)	0.0091(11)
*M*1 [a]	8*d*	0.17096(10)	0.12700(4)	0.32073(7)	0.0060(2)
*M*2 [b]	8*d*	0.00987(8)	0.09497(3)	0.81737(6)	0.0065(2)
Ge1	4*c*	0.9761(2)	1/4	0.0892(2)	0.0092(4)
Ge2	4*c*	0.2155(2)	1/4	0.63658(2)	0.0066(4)
Ge3	8*d*	0.1656(2)	0.96381(8)	0.53309(13)	0.0074(3)

[a] Refined as a statistical mixture of Gd and Mg in a ratio 77.2:22.8
[b] Refined as 100% Gd

Table S34. Selected crystallographic information for $Tb_{3.72(1)}Mg_{1.28}Ge_4$ at 298 K and 120 K.

empirical formula		$Tb_{3.72(1)}Mg_{1.28}Ge_4$
formula weight		912.32
space group		*Pnma* (No. 62)
λ, Å		0.71073
T, K	298	120
a, Å	7.1639(9)	7.154(3)
b, Å	14.651(2)	14.626(5)
c, Å	7.7515(10)	7.738(3)
V, Å^3, *Z* = 4	813.6(2)	809.6(5)
c/*a*	1.082	1.082
ρ_{calcd}, g cm^{-3}	7.448	7.485
μ (Mo Kα), cm^{-1}	464.20	466.48
R_1 [I > 2σ(I)]	0.0346	0.0296
wR_2 [I > 2σ(I)]	0.0498	0.0408
R_1 [all data]	0.0683	0.0607
wR_2 [all data]	0.0733	0.0638

Table S35. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Tb_{3.72(1)}Mg_{1.28}Ge_4$ at 298 K.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3394(7)	1/4	-0.0187(6)	0.0071(10)
*M*1 [a]	8*d*	0.16853(9)	0.12694(4)	0.32193(8)	0.0108(2)
*M*2 [b]	8*d*	0.00830(8)	0.09516(4)	0.81741(7)	0.0123(2)
Ge1	4*c*	0.9734(2)	1/4	0.0901(2)	0.0118(4)
Ge2	4*c*	0.2128(2)	1/4	0.6371(2)	0.0093(4)
Ge3	8*d*	0.1708(2)	0.96423(8)	0.5346(2)	0.0108(3)

Table S36. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Tb_{3.72(1)}Mg_{1.28}Ge_4$ at 120 K.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3379(6)	1/4	-0.0183(5)	0.0056(9)
*M*1 [a]	8*d*	0.16863(7)	0.12703(4)	0.32177(6)	0.0085(2)
*M*2 [b]	8*d*	0.00867(6)	0.09515(3)	0.8174(6)	0.0096(2)
Ge1	4*c*	0.9741(2)	1/4	0.0892(2)	0.0084(3)
Ge2	4*c*	0.2134(2)	1/4	0.6371(2)	0.0070(3)
Ge3	8*d*	0.17020(14)	0.96424(7)	0.53460(12)	0.0081(2)

[a] Refined as a statistical mixture of Tb and Mg in a ratio 85.9:14.1
[b] Refined as 100% Tb

Table S37. Selected crystallographic information for $Dy_{2.74(1)}Mg_{2.26}Ge_4$ at 298 K and 120 K.

empirical formula		$Dy_{2.74(1)}Mg_{2.26}Ge_4$
formula weight		790.21
space group		*Pnma* (No. 62)
λ, Å		0.71073
T, K	298	120
a, Å	7.008(2)	7.000(2)
b, Å	14.299(3)	14.269(4)
c, Å	7.662(2)	7.658(2)
V, Å^3, *Z* = 4	767.7(3)	764.9(4)
c/*a*	1.093	1.094
ρ_{calcd}, g cm^{-3}	6.840	6.865
μ (Mo Kα), cm^{-1}	418.43	419.99
R_1 [I > 2σ(I)]	0.0284	0.0169
wR_2 [I > 2σ(I)]	0.0575	0.0365
R_1 [all data]	0.0394	0.0198
wR_2 [all data]	0.0602	0.0374

Table S38. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Dy_{2.74(1)}Mg_{2.26}Ge_4$ at 298 K.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3421(7)	1/4	-0.0084(6)	0.0145(11)
*M*1 [a]	8*d*	0.17065(14)	0.12581(7)	0.32180(13)	0.0096(4)
*M*2 [b]	8*d*	0.00584(7)	0.09545(3)	0.81660(6)	0.0102(2)
Ge1	4*c*	0.9716(2)	1/4	0.1008(2)	0.0114(3)
Ge2	4*c*	0.2138(2)	1/4	0.6368(2)	0.0083(3)
Ge3	8*d*	0.1681(2)	0.96277(7)	0.53420(14)	0.0091(3)

Table S39. Atomic coordinates and equivalent displacement parameters (U_{eq}) for $Dy_{2.74(1)}Mg_{2.26}Ge_4$ at 120 K.

Atom	*Site*	*x*	*y*	*z*	U_{eq} (Å^2)
Mg	4*c*	0.3418 (4)	1/4	-0.0088(3)	0.0088(5)
*M*1 [a]	8*d*	0.17095(8)	0.12589(4)	0.32192(7)	0.0065(2)
*M*2 [b]	8*d*	0.00626(3)	0.09549(2)	0.81664(3)	0.0068(1)
Ge1	4*c*	0.97243(11)	1/4	0.10093(11)	0.0078(2)
Ge2	4*c*	0.21413(11)	1/4	0.63674(10)	0.0057(2)
Ge3	8*d*	0.16769(8)	0.96261(4)	0.53422(7)	0.0060(1)

[a] Refined as a statistical mixture of Dy and Mg in a ratio 36.7:63.3
[b] Refined as 100% Dy