

# Supporting Information

## Structure and Bonding in $\text{Yb}_4\text{MgGe}_4$ : $\text{Yb}^{2+}/\text{Yb}^{3+}$ Mixed-Valency and Charge Separation

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### Synthesis

All starting materials (ytterbium (> 99.9% metal basis, Ames Laboratory), germanium (lump, 99.999%, Acros) and magnesium (turnings, 99.8%, Alfa)) were stored and handled inside an Ar-filled glove box with controlled oxygen and moisture levels below 1 ppm or under vacuum. The elements were used as received.

Our original experiments were designed to produce a compound with different composition,  $\text{Yb}_2\text{MgGe}_2$ , isostructural with the recently reported  $\text{Yb}_2\text{InGe}_2$ .<sup>1</sup> Mg was chosen purposely in order to achieve a charge-balanced composition according to the Zintl-Klemm concept (*i.e.*  $(\text{Yb}^{2+})_2(\text{Mg}^{2+})(\text{Ge}^{3-})_2$  see text). The similarity of the  $\text{Mg}^{2+}$  and  $\text{In}^{3+}$  ionic radii were also taken into consideration:  $r(\text{Mg}^{2+}) = 0.86 \text{ \AA}$ ,  $r(\text{In}^{3+}) = 0.94 \text{ \AA}$  in these designed experiments.<sup>2</sup> Mixturea of the elements in a stoichiometric ratio of 2:1:2 (Yb:Mg:Ge) was loaded in welded Nb-containers, which were subsequently enclosed in evacuated fused silica tubes by flame sealing. The reaction temperature profile included heating to  $1100^\circ\text{C}$  at a rate of  $300^\circ\text{C}/\text{hour}$ , dwell at  $1100^\circ\text{C}$  for 20 h, followed by a quick cooling ( $-200^\circ\text{C}$ ) to  $700^\circ\text{C}$ . After the reaction was held for 20 days at  $700^\circ\text{C}$ , it was allowed to cool to room temperature over a period of 1 day.

The reactions loaded with this nominal composition produced a mixture of orthorhombic  $\text{YbMgGe}$ <sup>3</sup> and tetragonal  $\text{Yb}_{11}\text{Ge}_{10}$ <sup>4</sup> phases instead. To circumvent the formation of these compounds, new reactions were set-up using the same temperature profile but with different Yb:Mg:Ge ratios. One of them, where  $\text{Yb}:\text{Mg}:\text{Ge} = 4:1:4$  was found to yield quantitatively the title compound  $\text{Yb}_4\text{MgGe}_4$ . **Later, once the Mg tendency to mix predominantly with Yb on the Yb1 site was established, various on-stoichiometry reactions were set up in order to verify this and to establish the potential phase width.** In

all of these cases, mixtures of the elements in ratios of 3.75 : 1.25 : 4; 3.5 : 1.5 : 4; 3.25 : 1.75 : 4; and 3 : 2 : 4 were treated as described above. The Mg-richer reactions were found to yield the target compound in lower yields (based on powder X-ray diffraction), with  $\text{YbMgGe}$ ,<sup>3</sup>  $\text{Yb}_{11}\text{Ge}_{10}$ ,<sup>4</sup> and  $\text{Yb}_3\text{Ge}_5$ <sup>5</sup> as side products. The Mg-leaner nominal compositions produced virtually pure-phase materials, and the stoichiometry of the products was determined to be almost identical with the loading ratios (below).

$\text{Yb}_{5-x}\text{Mg}_x\text{Ge}_4$  crystallizes as shiny irregular crystals with metallic luster. The crystals are moderately stable in air, although signs of surface oxidation are visible after exposure to air.

### Structure Determination

Full spheres of single-crystal X-ray diffraction data were collected at room (*ca.* 20°C) and low (*ca.* -153°C) temperature on a Bruker SMART 1000 CCD diffractometer using monochromated Mo K $\alpha$  radiation. Single crystals of the title compound selected from different reactions were cut to suitable for data collection dimensions (below *ca.* 0.06 mm<sup>3</sup>), and were then mounted on glass fibers. The data collection included 0.4°  $\omega$ -scans with 10 sec exposure time per frame, and up to a diffraction angle  $2\theta_{\max} \sim 57^\circ$ . The data were collected using the SMART software package,<sup>6</sup> and were corrected for polarization effects and integrated using SAINT.<sup>7</sup> SADABS was used for absorption correction.<sup>8</sup> The structure was solved and refined on  $F^2$  with the aid of SHELXS and SHELXTL, respectively.<sup>9</sup> The orthorhombic  $\text{Sm}_5\text{Ge}_4$  type served as a model for the final refinements.<sup>10</sup> The refinements readily confirmed that the 4c site is exclusively occupied by Mg (Table S2 and S5), whereas the 8d site labeled herein as Yb1/Mg1 (Sm2 in  $\text{Sm}_5\text{Ge}_4$ ) site was refined as a statistical mixture of Yb and Mg. The amount of Mg on the Yb1 site can vary from 0 in  $\text{Yb}_4\text{MgGe}_4$ , to 12% in  $\text{Yb}_{3.75}\text{Mg}_{1.25}\text{Ge}_4$ , and to 28% in  $\text{Yb}_{3.45}\text{Mg}_{1.55}\text{Ge}_4$ , respectively, depending upon the experimental conditions. These subtle changes are evident from the difference in the cell volume (below). The different Mg content corresponds to valence electron concentrations ranging from 28 to 27.5, respectively, which agree well with the boundaries of electron deficiency established recently for the related  $\text{La}_{5-x}\text{Ca}_x\text{Ge}_4$  and  $\text{Ce}_{5-x}\text{Ca}_x\text{Ge}_4$  ( $3 < x < 3.8$ ) systems.<sup>11</sup> There is no evidence that Mg can substitute Yb on the other 8d site labeled Yb2 (Sm3 in  $\text{Sm}_5\text{Ge}_4$ ) or Ge on any of the three Ge sites as the occupancies of all deviated within 3 $\sigma$  when allowed to vary.

The temperature dependence of the cell axes and cell volume is as expected – the estimated volume expansion coefficient  $\beta$  is in the order of  $4 \times 10^{-5} \text{ K}^{-1}$  (Table S3). Important data collection and structure refinement parameters are listed in Tables S1, S2, S4 and S5, important interatomic distances are summarized in Table S3 and S6, respectively. Further information in the form of combined CIF is

available as Supporting Information, and has also been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) – depository numbers CSD 391359 for  $\text{Yb}_{4.04}\text{Mg}_{0.96}\text{Ge}_4$ ; CSD 391358 for  $\text{Yb}_{3.76}\text{Mg}_{1.24}\text{Ge}_4$ , and CSD 416252 for  $\text{Yb}_{3.45}\text{Mg}_{1.55}\text{Ge}_4$ , respectively.

## Magnetic Measurements

Field-cooled and zero-field cooled *dc* magnetization measurements were performed for the title compound using a Quantum Design MPMS SQUID magnetometer. The measurements were completed in the temperature range from 5 K to 300 K and in an applied magnetic field of 500 Oe. The samples (17.3 mg of  $\text{Yb}_4\text{MgGe}_4$  and 14.1 mg of  $\text{Yb}_{3.76}\text{Mg}_{1.24}\text{Ge}_4$ ) were enclosed in a custom-designed low background sample holder. The raw magnetization data were corrected for the holder contribution and converted to molar susceptibility.

## References

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6. SMART NT Version 5.63, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.
7. SAINT NT Version 6.45, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.
8. SADABS NT Version 2.10, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2001.
9. (a) SHELXS-97, Bruker Analytical Systems, Inc., Madison, WI, 1990; (b) SHELXTL Version 6.12, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.
10. There is an ongoing discussion whether the orthorhombic  $\text{Gd}_5\text{Si}_4$  and  $\text{Sm}_5\text{Ge}_4$  structures are identical or not. Although the two are isotypic (Pearson's symbol oP36, Villars, P.; Calvert, L. D. (Eds.) *Pearson's Handbook of Crystallographic Data for Intermetallic Compounds*, 2<sup>nd</sup> ed.; American Society for Metals: Materials Park, Ohio), the Tt-Tt bonding arrangements in both structures are markedly different – in  $\text{Gd}_5\text{Si}_4$  all Si atoms form dimers, while in  $\text{Sm}_5\text{Ge}_4$  only Ge2 are dimerized.
11. Wu, L.-M.; Kim, S.-H.; Seo, D.-K. *J. Am. Chem. Soc.* **2005**, *127*, 15682.

**Table S1.** Selected data collection and refinement parameters for  $\text{Yb}_4\text{MgGe}_4$ . Cell parameters reported herein were determined from single-crystal X-ray diffraction.

chemical formula	$\text{Yb}_{4.04(1)}\text{Mg}_{0.96(1)}\text{Ge}_4$	$\text{Yb}_{3.76(1)}\text{Mg}_{1.24(1)}\text{Ge}_4$	
formula weight	1012.78		
temperature, T (°C)	23	-153	23
space group, Z	<i>Pnma</i> (No. 62), 4		
unit cell parameters	$a = 7.155(2) \text{ \AA}$ $b = 14.769(5) \text{ \AA}$ $c = 7.688(2) \text{ \AA}$ $V = 812.5(4) \text{ \AA}^3$	$a = 7.133(3) \text{ \AA}$ $b = 14.737(6) \text{ \AA}$ $c = 7.681(3) \text{ \AA}$ $V = 807.4(6) \text{ \AA}^3$	$a = 7.1181(14) \text{ \AA}$ $b = 14.695(3) \text{ \AA}$ $c = 7.6639(15) \text{ \AA}$ $V = 801.7(3) \text{ \AA}^3$
radiation, $\lambda$ (Å)	Mo K $\alpha$ , 0.71073		
$\rho_{\text{calcd}}$ (g/cm <sup>3</sup> )	8.28	8.33	8.05
$\mu$ (cm <sup>-1</sup> )	605.6	609.4	581.7
final R1 ( $I > 2\sigma_I$ ) <sup>a</sup>	0.0352	0.0382	0.0244
final wR2 ( $I > 2\sigma_I$ ) <sup>b</sup>	0.0797	0.0808	0.0469
			0.0475

<sup>a</sup>  $R1 = \sum |F_o| - |F_c| / \sum |F_o|$

<sup>b</sup>  $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , and  $w = 1/[\sigma^2 F_o^2 + (AP)^2 + BP]$ ,  $P = (F_o^2 + 2F_c^2)/3$ ; A and B – weight coefficients.

**Table S2.** Atomic coordinates and equivalent displacement parameters  $U_{eq}$  ( $U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor) for  $\text{Yb}_4\text{MgGe}_4$ . Both data collections are completed at  $-153^\circ\text{C}$ .

Atom	Site	x	y	z	$U_{eq}$ ( $\text{\AA}^2$ )
<b><math>\text{Yb}_{4.04}\text{Mg}_{0.96}\text{Ge}_4</math></b>					
Mg <sup>*</sup>	4c	0.3438(7)	1/4	-0.0175(6)	0.0100(2)
Yb1	8d	0.17782(9)	0.12380(4)	0.32684(8)	0.0138(2)
Yb2	8d	0.01302(9)	0.09536(4)	0.81762(8)	0.0136(2)
Ge1	4c	0.9794(3)	1/4	0.1060(3)	0.0141(5)
Ge2	4c	0.2234(3)	1/4	0.6272(3)	0.0136(5)
Ge3	8d	0.1584(2)	0.9613(1)	0.5366(2)	0.0136(3)
<b><math>\text{Yb}_{3.76}\text{Mg}_{1.24}\text{Ge}_4</math></b>					
Mg	4c	0.3444(7)	1/4	-0.0144(6)	0.0100(1)
Yb1 <sup>**</sup>	8d	0.17694(7)	0.12374(3)	0.32664(6)	0.0070(2)
Yb2	8d	0.01290(7)	0.09580(3)	0.81738(6)	0.0085(2)
Ge1	4c	0.9781(2)	1/4	0.1068(2)	0.0081(4)
Ge2	4c	0.22225(2)	1/4	0.6270(2)	0.0077(4)
Ge3	8d	0.1591(2)	0.96110(8)	0.5361(1)	0.0087(3)

\* Mg is refined as a statistical mixture Mg : Yb = 95.6(2) : 4.4(2).

\*\* Yb1 is refined as a statistical mixture Yb : Mg = 88.0(3) : 12.0(3).

**Table S3.** Selected distances (Å) in Yb<sub>4</sub>MgGe<sub>4</sub>.

Yb <sub>4.04</sub> Mg <sub>0.96</sub> Ge <sub>4</sub> at 23 °C							Yb <sub>4.04</sub> Mg <sub>0.96</sub> Ge <sub>4</sub> at -153 °C							
$a = 7.155(2)$ Å, $b = 14.769(5)$ Å, $c = 7.688(2)$ Å; $V = 812.5(4)$ Å <sup>3</sup>							$a = 7.133(3)$ Å, $b = 14.737(6)$ Å, $c = 7.681(3)$ Å; $V = 807.4(6)$ Å <sup>3</sup>							
Ge1 —	Ge2	2.557(4)	Mg —	Ge1	2.767(5)		Ge1 —	Ge2	2.558(3)	Mg —	Ge1	2.767(6)		
	Mg	2.767(5)		Ge2	2.845(5)			Mg	2.767(6)		Ge2	2.836(6)		
2 × Yb1	2.893(2)			Ge2	2.890(5)		2 × Yb1	2.888(2)			Ge2	2.861(6)		
2 × Yb1	2.896(2)		2 × Ge3	3.148(2)		2 × Yb1	2.890(2)			2 × Ge3	3.141(2)			
2 × Yb2	3.195(2)		Ge1	3.286(5)		2 × Yb2	3.187(2)			Ge1	3.305(6)			
	Mg	3.286(5)	2 × Yb1	3.286(5)		Mg	3.305(6)			2 × Yb1	3.359(5)			
Ge2 —	Ge1	2.557(4)	2 × Yb1	3.438(4)		Ge1	2.558(3)			2 × Yb1	3.443(4)			
	Mg	2.845(5)	2 × Yb2	3.476(4)		Mg	2.836(6)			2 × Yb2	3.459(4)			
Mg	2.890(5)		2 × Yb2	3.526(3)		Mg	2.861(6)			2 × Yb2	3.516(4)			
Yb1	2.980(2)		Yb1 —	Ge3	2.818(2)		Yb1	2.981(2)		Yb1 —	Ge3	2.812(2)		
2 × Yb2	3.104(2)			Ge3	2.888(2)		2 × Yb2	3.096(2)			Ge3	2.890(2)		
2 × Yb2	3.115(2)			Ge1	2.893(2)		2 × Yb2	3.105(2)			Ge1	2.888(2)		
Ge3 —	Ge3	2.599(3)		Ge1	2.896(2)		Ge3 —	Ge3	2.593(3)		Ge1	2.890(2)		
	Yb1	2.818(2)		Ge3	2.912(2)			Yb1	2.812(2)			Ge3	2.902(2)	
Yb1	2.888(2)			Ge2	2.980(2)			Yb1	2.890(2)			Ge2	2.981(2)	
Yb1	2.912(2)			Mg	3.363(4)			Yb1	2.902(2)			Mg	3.359(4)	
Yb2	3.005(2)		Yb2 —	Ge3	3.005(2)			Yb2	3.003(2)		Yb2 —	Ge3	3.003(2)	
Yb2	3.103(2)			Ge2	3.103(2)			Yb2	3.097(2)			Ge2	3.096(2)	
Yb2	3.113(2)			Ge3	3.104(2)			Yb2	3.105(2)			Ge3	3.105(2)	
Mg	3.148(2)			Ge3	3.113(2)			Yb2	3.400(2)			Ge2	3.105(2)	
Yb2	3.411(2)			Ge2	3.115(2)						Ge1	3.187(2)		
				Ge1	3.195(2)						Ge3	3.411(2)		
				Ge3	3.411(2)						Mg	3.516(4)		
				Mg	3.476(4)						Mg	3.459(4)		
				Mg	3.526(4)									
Yb <sub>3.76</sub> Mg <sub>1.24</sub> Ge <sub>4</sub> at 23 °C							Yb <sub>3.76</sub> Mg <sub>1.24</sub> Ge <sub>4</sub> at -153 °C							
$a = 7.1181(14)$ Å, $b = 14.695(3)$ Å, $c = 7.664(2)$ Å; $V = 801.7(3)$ Å <sup>3</sup>							$a = 7.101(3)$ Å, $b = 14.649(6)$ Å, $c = 7.640(3)$ Å; $V = 794.6(5)$ Å <sup>3</sup>							
Ge1 —	Ge2	2.557(2)	Mg —	Ge1	2.764(5)		Ge1 —	Ge2	2.546(2)	Mg —	Ge1	2.761(5)		
	Mg	2.764(5)		Ge2	2.824(5)			Mg	2.761(5)		Ge2	2.819(6)		
2 × Yb1	2.874(1)			Ge2	2.879(5)		2 × Yb1	2.870(2)			Ge2	2.873(6)		
2 × Yb1	2.884(1)		2 × Ge3	3.131(1)		2 × Yb1	2.872(2)			2 × Ge3	3.116(2)			
2 × Yb2	3.179(1)			Ge1	3.271(5)		2 × Yb2	3.171(1)			Ge1	3.255(5)		
	Mg	3.271(5)	2 × Yb1	3.336(4)			Mg	3.255(2)			2 × Yb1	3.325(4)		
Ge2 —	Ge1	2.557(2)	2 × Yb1	3.420(4)		Ge2 —	Ge1	2.546(2)			2 × Yb1	3.409(4)		
	Mg	2.824(5)	2 × Yb2	3.457(4)			Mg	2.819(5)			2 × Yb2	3.448(4)		
Mg	2.879(5)		2 × Yb2	3.514(4)			Mg	2.873(5)			2 × Yb2	3.506(4)		
Yb1	2.976(1)		Yb1 —	Ge3	2.805(1)			Yb1	2.965(2)		Yb1 —	Ge3	2.798(1)	
2 × Yb2	3.079(1)			Ge3	2.882(1)		2 × Yb2	3.071(1)			Ge3	2.873(2)		
2 × Yb2	3.098(1)			Ge1	2.874(1)		2 × Yb2	3.088(2)			Ge1	2.870(2)		
Ge3 —	Ge3	2.600(2)		Ge1	2.884(1)		Ge3 —	Ge3	2.589(2)			Ge1	2.873(2)	
	Yb1	2.805(1)		Ge3	2.898(1)			Yb1	2.798(1)			Ge3	2.887(2)	
Yb1	2.882(2)			Ge2	2.976(1)			Yb1	2.873(2)			Ge2	2.965(2)	
Yb1	2.898(1)			Mg	3.336(4)			Yb1	2.887(2)			Mg	3.325(4)	
Yb2	2.994(1)		Yb2 —	Ge3	2.994(1)			Yb2	2.985(2)		Yb2 —	Ge3	2.985(2)	
Yb2	3.092(1)			Ge2	3.079(1)			Yb2	3.078(2)			Ge2	3.071(1)	
Yb2	3.104(1)			Ge3	3.092(1)			Yb2	3.096(1)			Ge3	3.079(2)	
Mg	3.131(1)			Ge3	3.104(1)			Mg	3.116(2)			Ge3	3.096(1)	
Yb2	3.387(1)			Ge2	3.098(1)			Yb2	3.385(2)			Ge2	3.088(2)	
				Ge1	3.179(1)						Ge1	3.171(1)		
				Ge3	3.387(1)						Ge3	3.385(2)		
				Mg	3.457(4)						Mg	3.448(4)		
				Mg	3.514(4)						Mg	3.506(4)		

**Note added as a proof.** While this manuscript was being reviewed, a new Mg-richer phase was synthesized. Selected structural information for  $\text{Yb}_{3.45}\text{Mg}_{1.55}\text{Ge}_4$  is listed follow:

**Table S4.** Selected data collection and refinement parameters for  $\text{Yb}_{3.45}\text{Mg}_{1.55}\text{Ge}_4$ . Cell parameters reported herein were determined from single-crystal X-ray diffraction.

chemical formula	$\text{Yb}_{3.45(1)}\text{Mg}_{1.55(1)}\text{Ge}_4$
formula weight	925.03
temperature, T (°C)	-153
space group, Z	<i>Pnma</i> (No. 62), 4
unit cell parameters	$a = 7.0599(11) \text{ \AA}$ $b = 14.565(2) \text{ \AA}$ $c = 7.6248(12) \text{ \AA}$ $V = 784.1(2) \text{ \AA}^3$
radiation, $\lambda$ (Å)	Mo K $\alpha$ , 0.71073
$\rho_{\text{calcd}}$ (g/cm <sup>3</sup> )	7.84
$\mu$ (cm <sup>-1</sup> )	558.5
final R1 ( $I > 2\sigma_I$ ) <sup>a</sup>	0.0241
final wR2 ( $I > 2\sigma_I$ ) <sup>b</sup>	0.0466

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

<sup>b</sup>  $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , and  $w = 1/[\sigma^2 F_o^2 + (0.0168P)^2 + 1.932P]$ ,  $P = (F_o^2 + 2F_c^2)/3$ .

**Table S5.** Atomic coordinates and equivalent displacement parameters  $U_{\text{eq}}$  for  $\text{Yb}_{3.45}\text{Mg}_{1.55}\text{Ge}_4$  (data collection again at -153 °C):

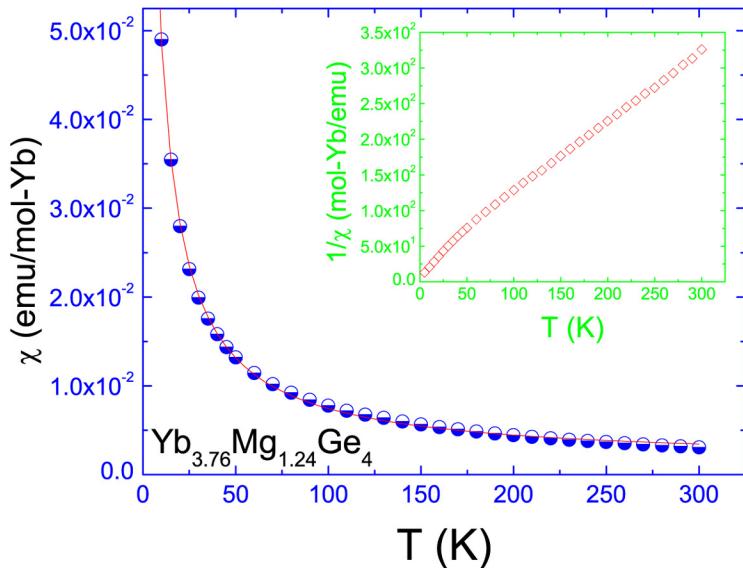
Atom	Site	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )
<b><math>\text{Yb}_{3.45}\text{Mg}_{1.55}\text{Ge}_4</math></b>					
Mg	4c	0.3444(6)	1/4	-0.0131(5)	0.0106(9)
Yb1 ***	8d	0.17549(7)	0.12399(3)	0.32614(6)	0.0067(2)
Yb2	8d	0.01155(5)	0.09556(3)	0.81733(5)	0.0082(1)
Ge1	4c	0.9771(2)	1/4	0.1059(2)	0.0076(3)
Ge2	4c	0.2210(2)	1/4	0.6288(2)	0.0078(3)
Ge3	8d	0.1612(1)	0.9614(1)	0.5350(1)	0.0084(2)

\* Yb1 is refined as a statistical mixture Yb : Mg = 72.1(2) : 27.9(2).

**Table S6.** Selected distances (Å) in  $\text{Yb}_{3.45}\text{Mg}_{1.55}\text{Ge}_4$ .

Yb <sub>3.76</sub> Mg <sub>1.24</sub> Ge <sub>4</sub> at -153 °C					
<i>a</i> = 7.0599(11) Å, <i>b</i> = 14.565(2) Å, <i>c</i> = 7.6248(12) Å; <i>V</i> = 784.1(2) Å <sup>3</sup>					
Ge1 —	Ge2 2.544(2)	Mg —	Ge1 2.747(4)		
	Mg 2.747(4)		Ge2 2.801(4)		
	2 × Yb1 2.855(1)		Ge2 2.866(4)		
	2 × Yb1 2.857(1)		2 × Ge3 3.101(1)		
	2 × Yb2 3.156(1)		Ge1 3.243(4)		
	Mg 3.243(4)		2 × Yb1 3.296(3)		
Ge2 —	Ge1 2.544(2)		2 × Yb1 3.388(4)		
	Mg 2.801(4)		2 × Yb2 3.448(4)		
	Mg 2.866(4)		2 × Yb2 3.506(4)		
	Yb1 2.967(1)	Yb1 —	Ge3 2.793(1)		
	2 × Yb2 3.052(1)		Ge3 2.856(1)		
	2 × Yb2 3.072(1)		Ge1 2.855(1)		
Ge3 —	Ge3 2.594(2)		Ge1 2.857(1)		
	Yb1 2.793(1)		Ge3 2.883(1)		
	Yb1 2.856(1)		Ge2 2.967(1)		
	Yb1 2.883(1)		Mg 3.388(4)		
	Yb2 2.964(1)	Yb2 —	Ge3 2.964(1)		
	Yb2 3.065(1)		Ge2 3.052(1)		
	Yb2 3.094(1)		Ge3 3.065(1)		
	Mg 3.101(1)		Ge3 3.094(1)		
	Yb2 3.3480(1)		Ge2 3.072(1)		
			Ge1 3.156(1)		
			Ge3 3.3480(1)		
			Mg 3.440(3)		
			Mg 3.501(3)		

**Figure 1S.** Magnetic susceptibility  $\chi(T)$  of  $\text{Yb}_{3.76}\text{Mg}_{1.24}\text{Ge}_4$  in an applied magnetic field of 500 Oe. Inset: inverse magnetic susceptibility  $\chi^{-1}(T)$ . Solid line indicates fit to the Curie-Weiss law  $\chi(T) = \chi_o + C/(T-\theta_p)$ .



The molar magnetic susceptibility ( $\chi = M/H$ , normalized per Yb) of 14.1 mg of polycrystalline  $\text{Yb}_{3.76}\text{Mg}_{1.24}\text{Ge}_4$  again does not show any magnetic order down to 10 K, and the temperature dependence of the molar susceptibility in the interval 10 – 300 K indicates a Curie-Weiss paramagnetic behavior. The  $\chi^{-1}(T)$  data above *ca.* 50 K were fit with the Curie-Weiss law, which resulted in an effective moment  $\mu_{\text{eff}} = 2.7 \mu_B/\text{Yb}$ . This value is in good agreement with the effective moment for the Mg-leaner  $\text{Yb}_4\text{MgGe}_4$  (see text). Nevertheless, in both cases, departures from the linear fit are clearly seen below *ca.* 30 K, therefore the data were fit with the modified Curie-Weiss. A nonlinear least-squares fit to  $\chi(T) = \chi_o + C/(T-\theta_p)$ , where  $\chi_o$  is the sum of the temperature-independent contributions, *e.g.* van Vleck paramagnetism, paramagnetism due to conduction electrons, and core-electron diamagnetism,  $C = N_A \mu_{\text{eff}}^2 / 3k_B$  is the Curie constant, and  $\theta_p$  is the Weiss temperature results in  $\chi_o = 1.3 \times 10^{-3} \text{ emu/mol}$ ,  $\theta_p = -4 \text{ K}$ , and an effective moment of  $2.2 \mu_B/\text{Yb}$ . Similar but slightly larger effective moment of  $2.3 \mu_B/\text{Yb}$  was derived for the Mg-leaner  $\text{Yb}_4\text{MgGe}_4$  by taking into account the temperature-independent contributions. This means that the ratio of magnetic  $\text{Yb}^{3+}$  to nonmagnetic  $\text{Yb}^{2+}$  in  $\text{Yb}_{3.76}\text{Mg}_{1.24}\text{Ge}_4$  is close to 0.9:1, compared to approx. 1:1 in  $\text{Yb}_4\text{MgGe}_4$ , which corroborates the analysis based upon bond

distances – Yb<sup>2+</sup> and Yb<sup>3+</sup> occupy different crystallographic sites in the structure and Mg substitutes preferentially the trivalent Yb's. Similar measurements and analysis of the effective moments of the Mg-richest phase Yb<sub>3.45</sub>Mg<sub>1.55</sub>Ge<sub>4</sub> were hampered by small amount of mixed-valent Yb<sub>3</sub>Ge<sub>5</sub><sup>5</sup> impurity.