Itinerant ferromagnet Re_{4-x}Mn_xGe_{7- δ} (*x* = 0.9–1.5, δ = 0.42–0.44) with incommensurate chimney-ladder structure stabilised at ambient pressure

Roman A. Khalaniya^{a,*}, Valeriy Yu. Verchenko^a, Alexey V. Bogach^{a, b}, Maxim Likhanov^a, Andrei V. Shevelkov^a

 ^a Department of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russia. E-mail: khalaniya@inorg.chem.msu.ru
 ^b Prokhorov General Physics Institute of the Russian Academy of Sciences, 119991 Moscow, Russia

Electronic Supporting Information for the manuscript

Experimental details

Synthesis and characterisation of powder samples

Re_{4-*x*}Mn_{*x*}Ge_{7- δ} was synthesised as a polycrystalline powder from the elements using two different techniques. Starting materials in both of them were Re powder (99.99%) and Mn (99.8%) and Ge chips (99.999%). The elements were weighed in the corresponding ratios with a total mass of 0.3–0.5 g. Several initial compositions were prepared with *x* and δ varying in the ranges of 0–3 and 0–1, respectively. Phase composition of the obtained samples was characterised by powder X-ray diffraction using Cu K α_1 radiation (Huber G670 diffractometer, $\lambda = 1.5406$ Å).

The first technique was the standard ampule method. The initial chemicals were placed into a small alumina crucible inside a silica ampule, which was then evacuated to the residual pressure of 10⁻³ Torr, sealed off, and annealed at 950°C or 1000°C for 2 days. After the first annealing, the samples were ground, pressed into pellets, and annealed again in sealed and evacuated silica ampules at 750°C or 800°C for 7 days. To prevent Mn from reacting with the silica tube walls, the bottom half of the tube was carbonised from the inside by pyrolysis of acetone. Lower annealing temperatures for the first and second stages (950°C and 750°C, respectively) led to inhomogeneous samples with their X-ray patterns

containing two distinct sets of peaks that belonged to $\text{Re}_{4-x}\text{Mn}_x\text{Ge}_{7-\delta}$. Samples obtained at higher temperatures exhibited no visible abnormalities in the shape of $\text{Re}_{4-x}\text{Mn}_x\text{Ge}_{7-\delta}$ Xray diffraction peaks. Further investigation using synchrotron radiation of the sample with nominal composition $\text{Re}_{2.5}\text{Mn}_{1.5}\text{Ge}_7$ (Fig. S1), however, showed pronounced asymmetry of the peaks (Fig. S1, inset) indicating that the Re/Mn ratio still noticeably varied within the volume of the sample. The synchrotron experiment was performed at the ID22 beamline ($\lambda = 0.354246(4)$ Å) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) [1]. The data were collected by nine Si [111] analyser crystals and an EIGER detector (EIGER2 X CdTe 2M-W) [2]. Measurements were conducted on the sample enclosed in a quartz capillary (0.4 mm in diameter) at room temperature.



Fig. S1. Synchrotron X-ray diffraction pattern of the Re_{2.5}Mn_{1.5}Ge₇ powder sample at room temperature. The region near the (2 1 1 0) peak is shown on the inset to highlight two chimney-ladder structures present in the sample, marked as NCL#1 and NCL#2. The upper black dots and black line represent the experimental diffraction pattern, the red line represents the calculated pattern. The red dotted lines on the inset show calculated patrial contributions from the phases and the background to the pattern. Peak positions are given lower by the short ticks. For the chimney-ladder structures, the main reflections of the Re subsystem are coloured in black, the main reflections of the Ge subsystem are magenta, the common reflections are blue, and the satellites are green. The difference plot is shown by the black line in the bottom part. In order to ensure an even Re/Mn distribution in the sample, the technique was changed with the initial samples now being treated in the arc-melting furnace. To obtain a single ingot, the elements were ground and pressed into a single pellet prior to the arc-melting. After the arc-melting, the ingots were ground and pressed into pellets again. Then the samples were annealed in sealed and evacuated silica ampules with carbonised walls at 800°C. X-ray diffraction analysis of the final samples does not show the presence of the second Nowotny phase, since the peaks appear to be narrow with slight asymmetry due to the instrument itself (Fig. S2). The detailed analysis of these samples using synchrotron radiation was not performed, thus a small degree of heterogeneity in the Re/Mn distribution cannot be ruled out completely.





In the case of all implemented techniques, the Re_{4-x}Mn_xGe_{7- δ} samples with higher Mn concentration ($x \ge 2$) contained large amounts of Ge and Mn-rich impurity Mn_{1-x}Re_xGe, while the samples with high Re concentration ($x \le 1$) contained Re-rich impurity Re₃Ge₇ supplemented by metallic Re. The samples within the range of 1 < x < 2 and $0 \le \delta \le 0.5$ also contained Ge, which amount was relatively low if initial δ was close to 0.5 but increased dramatically towards $\delta = 0$, whereas the samples with $0.5 \le \delta \le 1$ and within the same range of *x* contained Re and/or Mn_{1-x}Re_xGe. From this data, it could be concluded that the homogeneity range for the Mn doping is close to 1 < x < 2, whereas $\delta \approx 0.5$. However, since Mn is known for its relatively high volatility [3], the real homogeneity range is likely to be shifted towards the Re-rich side, which will be shown by the structural analysis in the next section. The effects of the Mn volatilisation are also noticeable during the synthetic process. The silica tube inner walls are covered with a thin yellow layer after the first annealing at 950°C or 1000°C. The samples intensively volatilise during the arc-melting, while the furnace chamber becomes visibly fogged. The EDX analysis of the obtained samples (Table S1), while not precise due to the rough surface of the samples even after pressing, also shows the general tendency for a lower Mn concentration in the chimney-ladder phase compared to that of the initial samples or a presence of Re-rich phases for $x \le 1$ consistent with the X-ray diffraction results. The EDX analysis also shows that the *x* and δ in the chimney-ladder phase stay in the ranges of 0.8–1.6 and 0.6–0.2, respectively. Microphotographs of the selected samples are presented in Fig. S3.

Table S1. Initial sample composition of selected sample against composition of the chimney ladder phase determined by the EDX analysis. Sample 1 was obtained using the first technique (first annealing – 1000°C, second annealing – 800°C). All other samples (2–8) were obtained using the arc-melting technique.

Sample	1	2	3	4
Initial	Re _{2.5}	Re ₃	Re _{2.5}	Re ₂
composition	M n _{1.5}	Mn_1	M n _{1.5}	Mn ₂
	Ge7	Ge _{6.57}	Ge _{6.57}	Ge _{6.57}
Composition	Re _{2.9(1)}	Re _{3.2(1)}	Re _{2.5(1)}	Re _{2.6(1)}
from EDX	Mn _{1.1(1)}	Mn _{0.8(1)}	Mn _{1.5(2)}	M n _{1.4(1)}
	Ge _{6.72(7)}	Ge _{6.67(6)}	Ge _{6.44(8)}	Ge _{6.8(2)}
Sample	5	6	7	8
Initial	Re _{1.5}	Re ₃	Re _{2.5}	Re ₂
composition	Mn _{2.5}	Mn_1	M n _{1.5}	Mn_2
	Ge _{6.57}	Ge ₆	Ge ₆	Ge ₆
Composition	Re _{2.4(1)}	Re _{3.0(2)}	Re _{2.8(1)}	Re _{2.6(1)}
from EDX	Mn _{1.6(1)}	Mn _{1.0(2)}	Mn _{1.2(1)}	Mn _{1.4(1)}
	Ge _{6.54(4)}	Ge _{6.57(1)}	Ge _{6.7(1)}	Ge _{6.47(4)}



Fig. S3. SEM raster images of the selected samples (Table S1) with following initial compositions: Re2.5Mn1.5Ge7 (1), Re3Mn1Ge6.57 (2), Re2.5Mn1.5Ge6.57 (3), Re2Mn2Ge6.57 (4), Re1.5Mn2.5Ge6.57 (5), Re3Mn1Ge6 (6), Re2.5Mn1.5Ge6 (7), Re2Mn2Ge6 (8). The phase areas were identified based on the EDX mapping and X-ray diffraction data. Light grey parts of the image belong to the chimney-ladder phase Re4- $_x$ Mn $_x$ Ge7- $_\delta$ or Re3Ge7. Re4- $_x$ Mn $_x$ Ge7- $_\delta$

composition determined by EDX is highlighted in red. Dark grey areas correspond to $Mn_{1-x}Re_xGe$ or Ge with the latter being slightly darker. White areas correspond to metallic Re.

Crystal structure refinement

The crystal structure was investigated using the high-resolution X-ray powder diffraction data obtained at the ID22 beam line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France, $\lambda = 0.35425$ Å) at room temperature for the Re_{2.5}Mn_{1.5}Ge₇ sample (Fig. S1, Sample 1 in Table S1) [1,2]. The structure refinement was performed using the Jana2006 software [4]. As the diffraction peaks were pronouncedly asymmetric, the diffraction pattern was fitted using two chimney-ladder structures (Fig. S1). The crystal structure was refined as a (3+1)-dimensional composite structure with transition metal and Ge substructures as its first and second components, respectively. As a starting model, we used the incommensurate crystal structure of FeGe_γ previously described Le Tonquesse et al [5]. The modulation vector *q* was defined as $q = c_T/c_{Ge}$, while the *I*4₁/*amd*(00 γ)00*ss* was chosen as the superspace group. The Ge subcell is derived from the T subcell by the *W*-matrix:

$$W_{Ge} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Each subcell contains one crystallographic site. The T atoms occupy the (0, 0, 0) site, and the Ge atoms occupy the (0.25, 0.25, 0.25) site. The displacement of the atoms was described using a positional modulation function of the n^{th} order $(n \le 5)$:

$$u(\nu) = \sum_{k=1}^{k} A^{k} \sin(2\pi k\nu) + B^{k} \cos(2\pi k\nu),$$

where A^k and B^k are the Fourier terms or the modulation wave amplitudes; k = 2, 4 for the T atoms, and k = 1-5 for the Ge atoms; *t* is the initial phase, $v = t + q \cdot x_3$ for the T atoms and $v = t + x_4/q$ for the Ge atoms, where x_3 and x_4 are the third and fourth coordinates, respectively. The Re/Mn ratio at the T site was also refined using the same type of the modulation function with the total occupancy kept at 1. Introducing the modulation function of a higher order did not improve the fit and resulted in the increased *R*-factor.

The crystal structure of Re_{4-x}Mn_xGe_{7- δ} was also studied by the laboratory X-ray Cu K α_1 radiation experiments on several other samples obtained using the arc-melting techniques in order to assess the homogeneity range (Fig. S2, Samples 3 and 4 in Table S1). Detailed crystallographic data and refinement parameters for Re_{4-x}Mn_xGe_{7- δ} are given in Table S2. The atomic parameters and refined modulation parameters are given in Tables S3 and S4. The *t*-plots for atomic displacement and interatomic distances are presented in Fig. S4 and S5. Crystallographic information files are deposited in the CCDC (ref. numbers 2271073–2271074) and available as a part of ESI.

Noticeably, the results of the structure refinement show discrepancy with the initial composition. This is due to several reasons. High volatility of Mn skews the final composition towards the Re-rich side, while the Ge excess in the case of Re_{2.5}Mn_{1.5}Ge₇ does result in the Ge admixture in the sample, as was noted earlier. Thus, the homogeneity range was concluded to be x = 0.9-1.5 and $\delta = 0.42-0.44$.

Sample (Table S1)	1		3	4	
Initial composition	Re _{2.5} Mn _{1.5} Ge ₇		Re _{2.5} Mn _{1.5} Ge _{6.57}	Re ₂ Mn ₂ Ge _{6.57}	
Composition from	Re _{2.9(1)}		Re _{2.5(1)}	Re _{2.6(1)}	
EDX	Mn _{1.1(1)}		Mn _{1.5(2)}	Mn _{1.4(1)}	
	Ge _{6.72(7)}		Ge _{6.44(8)} Ge _{6.8(2)}		
Refined	Re _{3.09(2)}	Re _{2.563(6)}	Re _{2.674(8)}	Re _{2.523(8)}	
composition	Mn _{0.91(2)}	Mn _{1.437(6)}	Mn _{1.326(8)}	Mn _{1.477(8)}	
	Ge _{6.574(1)}	Ge _{6.568(1)}	Ge _{6.577(1)}	Ge _{6.567(1)}	
Molar weight,	1102.2	1033	1068.9	1027.6	
g/mol					
Crystal system		teti	ragonal		
Space group		$I4_1/am$	d(00γ)00ss		
<i>a</i> , Å	5.86034(2)	5.848876(11)	5.85910(3)	5.85005(3)	
<i>с</i> _Т , Å	4.70446(2)	4.700312(11)	4.70099(3)	4.69733(3)	
c _{Ge} , Å	2.86264(2)	2.862351(11)	2.85903(3)	2.86138(3)	
<i>q</i> [001]	1.64340(5)	1.642116(15)	1.64426(3)	1.64163(3)	
$V_{\rm T},{ m \AA}^3$	161.5683(11)	160.7946(6)	161.3806(15)	160.7574(14)	
$V_{\text{Ge}}, \text{\AA}^3$	98.3134(11)	97.9192(6)	98.1478(15)	97.92531(14)	
$\rho_{calc}, g/cm^3$	11.327	10.668	10.985	10.615	
sample form		po	wder		
radiation	synchrotro	n radiation	Cu Ka1		
wavelength, Å	0.35	5425	1.5406		
temperature, K	298				
2θ range, °	2.001-	39.999	3.000-100.300		
h, k, l, m range	$0 \le h \le 11,$	$0 \le h \le 11,$	$0 \le h \le 4,$	$0 \le h \le 4,$	
	$0\leq k\leq 8,$	$0\leq k\leq 8,$	$0\leq k\leq 4,$	$0\leq k\leq 4,$	
	$0 \le l \le 16$	$0 \le l \le 15$	$0 \le l \le 12$	$0 \le l \le 12$	
	$-8 \le m \le 4$	$-8 \le m \le 4$	$-5 \le m \le 2$	$-5 \le m \le 2$	
N _{par}	3	3	41	43	
N _{ref}	1742	1753	226	277	
$R_p/R_{wp}, \%$	4.44/	/5.87	4.71/6.24	4.00/5.66	
GoF	3.	24	3.08	3.45	
$R[F^2>3\sigma(F^2)]$	2.88/4.35	2.75/4.23	3.11/2.34	3.36/5.25	
$/R_{w}(F^{2}), \%$					

Table S2. Crystallographic and refinement parameters for Re_{4-x}Mn_xGe_{7-δ}.

Sample (Table S1)	1		3	4	
Initial composition	Re _{2.5} Mn _{1.5} Ge ₇		Re _{2.5} Mn _{1.5} Ge _{6.57}	Re2Mn2Ge6.57	
Composition from	Re _{2.9(1)}		Re _{2.5(1)}	Re _{2.6(1)}	
EDX	Mn	1.1(1)	Mn _{1.5(2)}	Mn _{1.4(1)}	
	Ge _{6.72(7)}		Ge _{6.44(8)}	Ge _{6.8(2)}	
Refined composition	Re _{3.09(2)}	Re _{2.563(6)}	Re _{2.674(8)}	Re _{2.523(8)}	
	Mn _{0.91(2)}	Mn _{1.437(6)}	Mn _{1.326(8)}	Mn _{1.477(8)}	
	Ge _{6.574(1)}	Ge _{6.568(1)}	Ge _{6.577(1)}	Ge _{6.567(1)}	
Re/Mn position (x , y , z)	(0, 0, 0)				
Ge position (x , y , z)		(0.25,	0.25, 0.25)		
Re/Mn U _{iso}	0.00148(13)	0.00213(5)	0.00545(11)	0.00748(14)	
Ge U _{iso}	0.0034(5)	0.00632(16)	0.0159(3)	0.0157(4)	
Re occupancy	0.772(5)	0.6408(16)	0.669(2)	0.6307(19)	
Mn occupancy	0.228(5)	0.3592(16)	0.331(2)	0.3693(19)	

Table S3. Atomic parameters for Re_{4-x}Mn_xGe_{7-δ}

Table S4. Modulation parameters for $Re_{4-x}Mn_xGe_{7-\delta}$

Atom	n	x		у		Z	Occupancy
		А	В	А	В	В	А
Re/Mn	2					-0.0192(4)	0.162(9)
	4					0.0118(12)	-0.17(2)
Ge	1	0.07999(16)	A^1	0.07999(16)	$-A^1$		
	3	0.0071(2)	$-A^3$	0.0071(2)	A^3		
	4					-0.0323(13)	
	5	-0.0027(4)	A^5	-0.0027(4)	$-A^5$		
$Re_{2.563(6)}Mn_{1.437(6)}Ge_{6.568(1)}$							
Atom	n	x		У		Z	Occupancy
		А	В	А	В	В	А
Re/Mn	2					-0.02037(16)	0.227(2)
	4					0.0086(6)	-0.085(11)
Ge	1	0.07819(6)	A^1	0.07819(6)	$-A^1$		
	3	0.00732(8)	$-A^3$	0.00732(8)	A^3		
	4					-0.0221(4)	
Re 2.674(8)	Mn	1.326(8)Ge6.577(1)					
Atom	n	x		У		z	Occupancy
		А	В	А	В	В	А
					_		
Re/Mn	2					-0.0234(2)	0.182(2)
Re/Mn	2 4					-0.0234(2) 0.0109(7)	0.182(2) -0.062(8)
Re/Mn Ge	2 4 1	0.08008(7)	A ¹	0.08008(7)	-A ¹	-0.0234(2) 0.0109(7)	0.182(2) -0.062(8)
Re/Mn Ge	2 4 1 3	0.08008(7) 0.00745(12)	$\begin{array}{c} A^1 \\ -A^3 \end{array}$	0.08008(7) 0.00745(12)	$-A^1$ A^3	-0.0234(2) 0.0109(7)	0.182(2) -0.062(8)
Re/Mn Ge	2 4 1 3 4	0.08008(7) 0.00745(12)	A ¹ -A ³	0.08008(7) 0.00745(12)	$-A^1$ A^3	-0.0234(2) 0.0109(7) -0.0252(6)	0.182(2) -0.062(8)
Re/Mn Ge	2 4 1 3 4 5	0.08008(7) 0.00745(12) -0.0004(3)	A^{1} $-A^{3}$ A^{5}	0.08008(7) 0.00745(12) -0.0004(3)	$-A^{1}$ A^{3} $-A^{5}$	-0.0234(2) 0.0109(7) -0.0252(6)	0.182(2) -0.062(8)
Re/Mn Ge Re _{2.523(8)}	2 4 1 3 4 5 Mn	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8) Ge 6.567(1)	A^{1} $-A^{3}$ A^{5}	0.08008(7) 0.00745(12) -0.0004(3)	$-A^{1}$ A^{3} $-A^{5}$	-0.0234(2) 0.0109(7) -0.0252(6)	0.182(2) -0.062(8)
Re/Mn Ge Re _{2.523(8)} Atom	2 4 1 3 4 5 Mn <i>n</i>	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8)Ge6.567(1) x	A^{1} $-A^{3}$ A^{5}	0.08008(7) 0.00745(12) -0.0004(3) y	$-A^{1}$ A^{3} $-A^{5}$	-0.0234(2) 0.0109(7) -0.0252(6) z	0.182(2) -0.062(8) Occupancy
Re/Mn Ge Re _{2.523(8)} Atom	2 4 1 3 4 5 Mn <i>n</i>	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8)Ge6.567(1) x A	A^{1} $-A^{3}$ A^{5} B	0.08008(7) 0.00745(12) -0.0004(3) y A	$-A^{1}$ A^{3} $-A^{5}$ B	-0.0234(2) 0.0109(7) -0.0252(6) z B	0.182(2) -0.062(8) Occupancy A
Re/Mn Ge Re2.523(8) Atom Re/Mn	2 4 1 3 4 5 Mn <i>n</i> 2	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8)Ge6.567(1) x A	A^{1} $-A^{3}$ A^{5} B	0.08008(7) 0.00745(12) -0.0004(3) y A	$-A^{1}$ A^{3} $-A^{5}$ B	$-0.0234(2) \\ 0.0109(7) \\ -0.0252(6) \\ z \\ B \\ -0.0219(3) \\ -0.0219(3$	0.182(2) -0.062(8) Occupancy A 0.198(2)
Re/Mn Ge Re2.523(8) Atom Re/Mn	2 4 1 3 4 5 Mn <i>n</i> 2 4	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8)Ge6.567(1) x A	A^{1} $-A^{3}$ A^{5} B	0.08008(7) 0.00745(12) -0.0004(3) y A	$-A^{1}$ A^{3} $-A^{5}$ B	-0.0234(2) $0.0109(7)$ $-0.0252(6)$ z B $-0.0219(3)$ $0.0170(4)$	0.182(2) -0.062(8) Occupancy A 0.198(2)
Re/Mn Ge Re _{2.523(8)} Atom Re/Mn Ge	2 4 1 3 4 5 Mn <i>n</i> 2 4 1	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8)Ge6.567(1) x A 0.07907(7)	A^{1} $-A^{3}$ A^{5} B A^{1}	0.08008(7) 0.00745(12) -0.0004(3) y A 0.07907(7)	$-A^{1}$ A^{3} $-A^{5}$ B $-A^{1}$	$ \begin{array}{c} -0.0234(2) \\ 0.0109(7) \\ -0.0252(6) \\ \hline z \\ B \\ -0.0219(3) \\ 0.0170(4) \\ \end{array} $	0.182(2) -0.062(8) Occupancy A 0.198(2)
Re/Mn Ge Re _{2.523(8)} Atom Re/Mn Ge	2 4 1 3 4 5 Mn 2 4 1 3	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8)Ge6.567(1) x A 0.07907(7) 0.00647(12)	A^{1} $-A^{3}$ A^{5} B A^{1} $-A^{3}$	0.08008(7) 0.00745(12) -0.0004(3) y A 0.07907(7) 0.00647(12)	$-A^{1}$ A^{3} $-A^{5}$ B $-A^{1}$ A^{3}	$ \begin{array}{r} -0.0234(2) \\ 0.0109(7) \\ -0.0252(6) \\ \hline z \\ B \\ -0.0219(3) \\ 0.0170(4) \\ \end{array} $	0.182(2) -0.062(8) Occupancy A 0.198(2)
Re/Mn Ge Re _{2.523(8)} Atom Re/Mn Ge	2 4 1 3 4 5 Mn 2 4 1 3 4	0.08008(7) 0.00745(12) -0.0004(3) 1.477(8)Ge6.567(1) x A 0.07907(7) 0.00647(12)	A^{1} $-A^{3}$ A^{5} B A^{1} $-A^{3}$	0.08008(7) 0.00745(12) -0.0004(3) y A 0.07907(7) 0.00647(12)	$-A^{1}$ A^{3} $-A^{5}$ B $-A^{1}$ A^{3}	-0.0234(2) $0.0109(7)$ $-0.0252(6)$ z B $-0.0219(3)$ $0.0170(4)$ $-0.0242(6)$	0.182(2) -0.062(8) Occupancy A 0.198(2)

 $Re_{3.09(2)}Mn_{0.91(2)}Ge_{6.574(1)}$



Fig. S4. Modulation of the atomic positions in Re_{4-x}Mn_xGe_{7- δ} (x = 1.437(6), $\delta = 0.432(1)$, Sample 1, Tables S2, S3, and S4) versus the initial phase *t*.



Fig. S5. Modulation of the T-Ge and T-T distances and the Mn occupancy (a), modulation of the Ge-T and Ge-Ge distances (b), and modulation of the atomic positions (c) in Re_{4-x}Mn_xGe_{7- δ} (*x* = 1.326(6), δ =0.423(1), Sample 3, Tables S2, S3, and S4) versus the initial phase *t*.

Electronic structure calculations

Theoretical calculations of the electronic structure were performed using the tightbinding approach in the TB-LMTO-ASA package [6]. As a model for the incommensurate structure of Re_{4-x}Mn_xGe_{7- δ}, an approximant ordered structure Re₇Mn₄Ge₁₈, with Mn and Re atoms occupying different sites (Fig. S6a) was used. This model was constructed from the approximant obtained from Jana2006 (Fig. S6b) based on the modulation parameters for Re_{4-x}Mn_xGe_{7- δ} (*x* = 1.437(6), δ =0.432(1), Sample 1, Tables S2, S3, and S4). The space group was set to *I*-42*d* to reduce the number of variable parameters. The atomic coordinates were slightly altered to prevent atomic overlap or short atomic distances. Mn and Re sites were chosen based on the Mn/Re ratio at the specific positions. The geometry optimisation was not performed, as TB-LMTO-ASA does not support this procedure [6]. For the exchange-correlation energy, the Perdew-Wang 92 functional [7] was used. Reciprocal space integration was performed on a $16 \times 16 \times 8$ *k*-points grid using the tetrahedron method [8]. Both non-magnetic and spin-polarised calculations were performed. Several other Mn/Re distributions were also tested, but yielded practically identical results with the overall magnetic moment differing by no more than 0.2 µ_B. The atomic and orbital projected density of states for the non-magnetic model is presented in Fig. S7.



Fig. S6. Single unit cell of the Re₇Mn₄Ge₁₈ approximant (a) used in the theoretical calculations, 11-cell approximant (b) constructed from the modulation parameters for Re_{4-x}Mn_xGe_{7- δ} (*x* = 1.437(6), δ =0.432(1), Sample 1, Tables S2, S3, and S4).



Fig. S7. Calculated projected densities of states for Re (a), Mn, (b), Ge (c) atoms in the Re7Mn4Ge18 approximant for the non-magnetic model.

Magnetisation measurements

For the magnetic measurement, one of the samples with the initial composition $Re_{2.5}Mn_{1.5}Ge_{6.57}$ (Sample 3, Table S1) obtained using the arc-melting technique was chosen. This sample contained only small amount (about 5%) of a diamagnetic impurity in the form of Ge. The composition of the Nowotny chimney-ladder phase was refined to be $Re_{2.7}Mn_{1.3}Ge_{6.58}$ (Sample 3, Table S2). Magnetisation of the $Re_{2.7}Mn_{1.3}Ge_{6.58}$ powder

sample was measured using a Magnetic Properties Measurement System (MPMS-XL5 SQUID, Quantum Design) in various external magnetic fields up to 5 T in the temperature range of 2–300 K. Fisher's heat capacity plot for Re_{2.7}Mn_{1.3}Ge_{6.58} obtained from the measurements is given in Fig. S8. The results of the Curie-Weiss approximation of the paramagnetic region are presented in Fig. S9.



Fig. S8. Fisher's heat capacity curve for the Re_{2.7}Mn_{1.3}Ge_{6.58} powder (Sample 3, Table S2) calculated from the magnetisation data measured in 1 kOe applied field.



Fig. S9. Inverse magnetic susceptibility for the Re_{2.7}Mn_{1.3}Ge_{6.58} powder (Sample 3, Table S2). Black circles represent experimental results, red line is the Curie-Weiss fit.

References

- V. Y. Verchenko and O. Grendal, Metal-to-insulator electronic phase transition in the Re₃Ge₇ endohedral cluster compound [Data set], European Synchrotron Radiation Facility, 2024. doi.org/10.15151/ESRF-ES-395241975
- C. Dejoie, M. Coduri, S. Petitdemange, C. Giacobbe, E. Covacci, O. Grimaldi, P.-O. Autran, M.W. Mogodi, D. Šišak Jung and A.N. Fitch, Combining a nine-crystal multianalyser stage with a two-dimensional detector for high-resolution powder X-ray diffraction. *J. Appl. Crystallogr.*, 2018, **51**, 1721.
- S. T. Ali, K.S. Rao, C. Laxman, N.R. Munirathnam and T.L. Prakash, Preparation of high pure zinc for electronic applications using selective evaporation under vacuum. *Sep. Purif. Technol.*, 2012, **85**, 178–182.
- 4. V. Petricek, M. Dusek and L. Palatinus, Crystallographic computing system JANA2006: general features. *Z. für Kristallogr. Cryst. Mater.*, 2014, **229**, 345–352.
- 5. S. Le Tonquesse, C. Hassam, Y. Michiue, Y. Matsushita, M. Pasturel, T. Mori, T. S. Suzuki and D. Berthebaud, Crystal structure and high temperature X-ray diffraction study of thermoelectric chimney-ladder FeGe_{γ} ($\gamma \approx 1.52$). *J. Alloys Compd.*, 2020, **846**, 155696.
- O. Jepsen, A. Burkhardt and O. K. Andersen, The Program TB-LMTO-ASA, version 4.7. Max-Planck-Institut f
 ür Festkörperforschung, Stuttgart, 1999.
- 7. J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electrongas correlation energy. *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **45**, 13244.
- 8. P. E. Blöchl, O. Jepsen and O. K. Andersen, Improved tetrahedron method for Brillouinzone integrations. *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 16223.