Supporting Information:

Investigating the $A_{n+1}B_nX_{3n+1}$ Homologous Series: A New Platform for Studying Magnetic Praseodymium Based Intermetallics

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Disorder Model for $Pr_4Co_{3+x}Ge_{10-y}Sn_y$ and $Pr_5Co_{4+x}Ge_{13-y}Sn_y$

The disorder of the Pr2 local environment in $Pr_4Co_{3+x}Ge_{10-y}Sn_y$ and Pr1/Pr3 environment in $Pr_5Co_{4+x}Ge_{13-y}Sn_y$ were modelled as a mixture of Sn and Co-Ge dimers with Co vacancies. The total occupancy of all configurations was constrained to unity, since without this constraint total occupancy remained approximately 98%. Additionally, without either the Co-Ge dimer or Sn atom a void of approximately 10 x 4 x 4 $Å^3$ would remain, which without distortions occurring elsewhere in the structure is chemically unreasonable in an intermetallic system. Additionally, the atomic displacement parameters of Co, Ge, and Sn were set equal to prevent unrealistic features, such as overlapping atomic positions. Mixing of Ge and Sn was considered on the Sn sites of both structures but did not result in significant improvement in the refinement quality.

Table S1. Crystallographic Data, Data Collection, and Refinement Parameters

Empirical formula	$Pr_4Co_{3.25(3)}Ge_{9.50(1)}Sn_{0.469(4)}$	$Pr_5Co_{4.22(2)}Ge_{12.48(1)}Sn_{0.519(7)}$
Space group	*Cmcm* (no. 63)	*Cmmm* (no. 65)
Lattice parameters		
a (Å)	4.3091(12)	4.2899(9)
b (Å)	35.750(9)	45.487(8)
c (Å)	4.2807(11)	4.3115(7)
Volume [$Å^3$]	659.4(3)	841.3(3)
Z	2	2
Density [g/cm^3]	7.575	7.583
Absorption coefficient [mm^{-1}]	40.59	40.82
F(000)	1306	1669

Crystal size [mm^3]	0.01 x 0.01 x 0.02	0.02 x 0.12 x 0.14
θ range [˚]	2.3 – 30.4	2.7 – 30.5
Index range		
h	-6 → 6	-6 → 6
k	-50 → 50	-64 → 64
l	-6 → 6	-6 → 6
Number of reflections	10797	16553
Unique reflections	630	817
parameters/restraints	42/2	55/2
R_{int}	0.052	0.072
$\Delta\rho_{max/min}$ ($e^-/Å^3$)	1.81/-2.41	3.21/-3.40
GoF	1.13	1.16
$R\ [F^2 > 2\sigma(F^2)]$	0.033	0.033
$wR_2\ (F^2)$	0.068	0.094

$R = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \left\{\sum w\left[(F_o)^2 - (F_c)^2\right]^2 / \sum w\left[(F_o)^2\right]^2\right\}^{1/2}$

Table S2. Atomic Coordinates and Displacement Parameters for $Pr_4Co_{3+x}Ge_{10-y}Sn_y$ Compared to $Eu_4Ni_{4-x}Sn_{10}$

Site Label	Wyckoff	*x*	*y*	*z*	U_{eq} (Å^2)	Occupancy
$Eu_4Ni_{2.98(2)}Sn_{10}$[1]						
Eu1	4*c*	0	0.81769(1)	1/4	0.0123(1)	1
Eu2	4*c*	0	0.54802(1)	1/4	0.0129(1)	1
Ni2	4*c*	0	0.91216(3)	1/4	0.0111(3)	1
Sn1	4*c*	0	0.97762(2)	1/4	0.0138(2)	1
Sn2	4*c*	0	0.25017(3)	1/4	0.0258(2)	1
Sn3	4*c*	0	0.38403(2)	1/4	0.0137(2)	1
Sn4	4*c*	0	0.115188(2)	1/4	0.0135(2)	1
Ni1	4*c*	0	0.72828(7)	1/4	0.0185(15)	0.482(7)
Sn5A	4*c*	0	0.66797(5)	1/4	0.0143(2)	0.528(2)
Sn5B	4*c*	0	0.68132(5)	1/4	0.0143(2)	0.472(2)
$Pr_4Co_{3.25(3)}Ge_{9.50(1)}Sn_{0.469(4)}$						
Pr1	4*c*	0	0.81937(2)	1/4	0.01133(18)	1
Pr2	4*c*	0	0.54728(2)	1/4	0.00817(17)	1
Co2	4*c*	0	0.91305(5)	1/4	0.0076(3)	1
Ge1	4*c*	0	0.97881(4)	1/4	0.0084(3)	1
Ge2	4*c*	0	0.25012(4)	1/4	0.0124(3)	1
Ge3	4*c*	0	0.38576(4)	1/4	0.0096(3)	1
Ge4	4*c*	0	0.11415(4)	1/4	0.0095(3)	1
Co1A	4*c*	0	0.72387(11)	1/4	0.0139(4)	0.577(7)
Ge5A	4*c*	0	0.66098(9)	1/4	0.0139(4)	0.667(3)
Co1B	4*c*	0	0.6386(8)	1/4	0.0139(4)	0.050(6)
Ge5B	4*c*	0	0.7010(6)	1/4	0.0139(4)	0.084(3)
Sn1	4*c*	0	0.68013(16)	1/4	0.0139(4)	0.248(2)

Table S3. Atomic Coordinates and Displacement Parameters for $Pr_5Co_{4+x}Ge_{13-y}Sn_y$ Compared to $Ce_5Co_{4+x}Ge_{13-y}Sn_y$

Site Label	Wyckoff	*x*	*y*	*z*	U_{eq} (Å^2)	Occupancy
$Ce_5Co_{4.44}Ge_{12.44}Sn_{0.56}$ [2]						
Ce1	4*j*	0	0.39185(2)	1/2	0.00763(19)	1
Ce2	4*i*	0	0.21286(2)	0	0.00650(18)	1
Ce3	2*a*	0	0	0	0.0098(2)	1
Co1	4*j*	0	0.31873(3)	1/2	0.0055(3)	1
Ge1	4*j*	0	0.05303(3)	1/2	0.0098(2)	1
Ge2	4*j*	0	0.16017(2)	1/2	0.0074(2)	1
Ge3	4*j*	0	0.26676(2)	1/2	0.0061(2)	1
Ge5	4*i*	0	0.33979(2)	0	0.0071(2)	1
Ge6	4*i*	0	0.44698(3)	0	0.0100(3)	1
Co2	4*i*	0	0.07341(4)	0	0.0107(4)	0.866(6)
Ge4	4*i*	0	0.12335(5)	0	0.0099(3)	0.866(6)
Sn1	4*i*	0	0.1081(3)	0	0.020(2)	0.134(6)
Co3	4*j*	1/2	0.03342(10)	1/2	0.0139(5)	0.3560(16)
Ge7	4*j*	1/2	-0.01576(8)	1/2	0.0139(5)	0.3560(16)
Sn2	2*c*	1/2	0	1/2	0.0139(5)	0.288(3)
$Pr_5Co_{4.22(2)}Ge_{12.48(1)}Sn_{0.519(7)}$						
Pr1	4*j*	0	0.39170(2)	1/2	0.00680(19)	1
Pr2	4*i*	0	0.21302(2)	0	0.00550(18)	1
Pr3	2*a*	0	0	0	0.0087(2)	1
Co1	4*j*	0	0.31849(3)	1/2	0.0047(3)	1
Ge1	4*j*	0	0.05311(3)	1/2	0.0094(3)	1
Ge2	4*j*	0	0.16042(2)	1/2	0.0064(2)	1
Ge3	4*j*	0	0.26668(2)	1/2	0.0055(2)	1
Ge5	4*i*	0	0.33959(2)	0	0.0060(2)	1
Ge6	4*i*	0	0.44685(2)	0	0.0096(3)	1

Co2	4*i*	0	0.07342(4)	0	0.0090(3)	0.829(5)
Ge4	4*i*	0	0.12331(3)	0	0.0090(3)	0.8756(17)
Sn1	4*i*	0	0.10813(13)	0	0.0090(3)	0.1244(17)
Co3	4*j*	1/2	0.03376(13)	1/2	0.0132(5)	0.282(5)
Ge7	4*j*	1/2	−0.01560(8)	1/2	0.0132(5)	0.3651(11)
Sn2	2*c*	1/2	0	1/2	0.0132(5)	0.270(2)

References

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2. Weiland, A.; Wei, K.; McCandless, G. T.; Baumbach, R. E.; Chan, J. Y., Fantastic n = 4: $Ce_5Co_{4+x}Ge_{13-y}Sn_y$ of the $A_{n+1}M_nX_{3n+1}$ Homologous Series. *J. Chem. Phys.* **2021,** *154*, 114707.