Electronic Supplementary Information for Dalton Transactions

Supporting Information

Interpenetrating Icosahedra Chains Based Zinc-Rich Ternary Phases $Ru_{4.0}Sn_{2.9}Zn_{11.6}$ and $Ru_{3.0}Sb_{0.97}Zn_{11.0}$: Synthesis, Structures and Physical Properties

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Table S1 Anisotropic displacement parameters (in $Å^2$) for $Ru_{3.0}Sb_{0.97}Zn_{11.0}$ and $Ru_4Sn_{2.9}Zn_{11.6}$.

$Ru_{3.0}Sb_{0.97}Zn_{11.0}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0.0166(4)	0.0111(4)	0.0048(4)	0.0090(3)	0.00000	0.00000
Zn6	0.0166(4)	0.0111(4)	0.0048(4)	0.0090(3)	0.00000	0.00000
Ru1	0.0221(5)	0.0027(4)	0.0040(4)	0.00000	0.00000	0.00000
Ru2	0.0057(3)	0.0021(3)	0.0039(3)	0.00000	0.00000	-0.0003(2)
Zn1	0.0069(6)	0.0094(7)	0.0077(6)	0.00000	0.00000	-0.0040(5)
Zn2	0.0093(3)	0.0158(4)	0.0176(4)	0.0041(3)	-0.0024(3)	-0.0047(3)
Zn3	0.0180(5)	0.0059(5)	0.0172(5)	0.00000	0.00000	-0.0049(4)
Zn4	0.0263(7)	0.0403(9)	0.0254(6)	0.0255(7)	-0.0162(6)	-0.0212(6)
Zn5	0.082(2)	0.0269(12)	0.0177(10)	0.00000	0.00000	0.0161(9)

$Ru_4Sn_{2.9}Zn_{11.6}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	0.0089(4)	0.0084(4)	0.0114(4)	0.0029(2)	0.0030(3)	0.0010(2)
Zn8	0.0089(4)	0.0084(4)	0.0114(4)	0.0029(2)	0.0030(3)	0.0010(2)
Ru1	0.0018(4)	0.0045(5)	0.0056(5)	0.00000	0.0018(4)	0.00000
Ru2	0.0029(5)	0.0062(4)	0.0065(5)	0.00000	0.0021(4)	0.00000
Zn1	0.0115(9)	0.0043(8)	0.0094(9)	0.00000	0.0039(8)	0.00000
Zn2	0.0081(5)	0.0020(5)	0.0061(5)	0.0007(3)	0.0036(4)	0.0004(3)
Zn3	0.0027(8)	0.0120(9)	0.0120(9)	0.00000	0.0000(7)	0.00000
Zn4	0.0065(7)	0.0132(7)	0.0163(8)	0.00000	0.0066(6)	0.00000
Zn5	0.0330(12)	0.0205(11)	0.0169(10)	0.0207(8)	0.0177(8)	0.0124(7)
Zn6	0.032(3)	0.052(3)	0.0206(19)	0.00000	-0.0198(16)	0.00000

Table S2. Crystallographic and technical data of the single crystal structure refinements of annealed $Ru_4Sn_{2.9}Zn_{11.5}$.

Crystallographic data	
Chemical formula	$Ru_4Sn_{2.88}Zn_{11.73}$
M_r	1513.06
Space group (no.), Z	$C2/m$ (12), 2
Pearson symbol	$mC46–\delta$
a / Å	6.8307(14)
b / Å	7.9848(16)
c / Å	11.047(2)
β / °	97.50(3)
V/ Å ^{3}	597.4(2)
D_c/g cm^{-3}	8.370
μ/mm^{-1}	33.527
Data collection	
Crystal size/mm^3	0.07 × 0.17 × 0.19
Diffractometer	IPDS (Stoe & Cie)
Radiation	MoK_α
Monochromator	Graphite
Crystal−IP distance/mm	60
T/K	293(2)
φ_{min}–φ_{max}; $\Delta\varphi$/°	0−250; 1.2
θ_{max}/°	28.06
Reflections measured	3859
Index range, hkl	−8 to 9, −10 to 10, −14 to 14
Data reduction	
Data reduction/	IPDS-Software[30] / numerical
Absorption correction	X-RED[31], X-SHAPE[32]
Min/Max transmission	0.0277 / 0.0998
Unique reflections	767
R_{int}	0.2216
Refinement	
Programs	SHELXTL version 6.10
Refinement method	Full matrix least squares on F^2
No. used reflections	767
No. variables	58
Obs. reflection ($I_o > 2\sigma(I_o)$)	598
$R(F)$ [a] ($I_o > 2\sigma(I_o)$)	0.0998
$R(F)$ (all data)	0.1116
$wR(F^2)$ [b] (all data)	0.2387
Goodness of fit (F^2)	1.004
$\Delta\rho_{min}/\Delta\rho_{max}$/ e Å^3	−6.301 / 4.274

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table S3. Atomic coordinates and equivalent displacement parameters (Å^2) for annealed $Ru_4Sn_{2.9}Zn_{11.5}$.

Compound	Atom	Wyckoff	*x*	*y*	*z*	U_{eq} [a]	Occupancy ≠ 1
$Ru_4Sn_{2.8}Zn_{11.5}$	M(Sn/Zn8)	8*j*	0.18203(15)	0.31645(16)	0.60914(11)	0.0094(3)	0.72/0.20
	Ru1	4*i*	0.14869(19)	½	0.39366(14)	0.0039(3)	
	Ru2	4*i*	0.23213(19)	½	0.82701(14)	0.0051(3)	
	Zn1	2*b*	0	½	0	0.0082(4)	
	Zn2	8*j*	0.07742(2)	0.29822(2)	0.19655(15)	0.0052(3)	
	Zn3	2*c*	0	0	½	0.0090(4)	
	Zn4	4*i*	0.42288(3)	½	0.25173(2)	0.0116(4)	
	Zn5	4*e*	¼	¼	0	0.0222(8)	0.973
	Zn6	2*a*	0	0	0	0.037(2)	0.981

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4 Anisotropic displacement parameters (in Å^2) for annealed $Ru_4Sn_{2.9}Zn_{11.6}$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	0.0160(5)	0.0248(7)	0.0245(6)	0.0044(4)	-0.0046(4)	0.0010(5)
Zn8	0.0160(5)	0.0248(7)	0.0245(6)	0.0044(4)	-0.0046(4)	0.0010(5)
Ru1	0.0093(5)	0.0205(8)	0.0167(7)	0.00000	-0.0056(5)	0.00000
Ru2	0.0090(5)	0.0200(7)	0.0182(7)	0.00000	-0.0052(5)	0.00000
Zn1	0.0156(12)	0.0211(16)	0.0238(16)	0.00000	-0.0014(11)	0.00000
Zn2	0.0176(6)	0.0201(8)	0.0211(8)	0.0028(6)	-0.0032(6)	0.0001(7)
Zn3	0.0101(12)	0.0328(18)	0.0287(17)	0.00000	-0.0096(11)	0.00000
Zn4	0.0139(9)	0.0304(13)	0.0302(13)	0.00000	0.0000(8)	0.00000
Zn5	0.0371(14)	0.0338(16)	0.0304(16)	0.0158(11)	0.0093(10)	0.0096(12)
Zn6	0.032(2)	0.058(3)	0.037(2)	0.00000	-0.0209(16)	0.00000

Table S5. Interatomic distances (Å) in the structures of annealed $Ru_4Sn_{2.9}Zn_{11.6}$.

atomic pair	distance	atomic pair	distance	atomic pair	distance
M − Ru1	2.690(2)	Zn1 −Zn5 ×4	2.627(0)	Zn4 − Ru1	2.595(18)
Zn2	2.688(39)	Ru2 ×2	2.638(34)	Ru2	2.616(23)
Ru1	2.779(6)	Zn2 ×4	2.700(13)	Zn3	2.725(16)
Ru1	2.781(1)	Zn6 ×2	3.415	Zn2 ×2	2.706(7)
Ru2	2.801(9)	Zn2 − Zn5	2.631(29)	Zn2 ×2	2.857(15)
M	2.896(23)	Ru2	2.644(6)	Zn6	2.897(15)
M	2.931(2)	M	2.688(39)	M ×2	3.090(11)
Zn2	2.960(38)	Zn1	2.700(10)	M ×2	3.273
Zn3	2.999(15)	Ru1	2.702(11)	Zn5 − Zn6 ×2	2.627(0)
Zn3	3.000(26)	Zn4	2.706(7)	Zn1 ×2	2.627(0)
Zn4	3.090(14)	Ru2	2.742(4)	Zn2 ×2	2.631(29)
M	3.230(19)	Zn4	2.857(15)	Ru2 ×2	2.755(3)
Zn4	3.273	Zn5	2.932(49)	Zn2 ×2	2.932(49)
Ru1 − Zn3	2.530(33)	M	2.960(38)	Zn5 ×2	3.415
Zn4	2.595(34)	Zn2	3.223	Zn6 − Ru2 ×2	2.467(42)
M ×2	2.690(2)	Zn6	3.219	Zn5 ×4	2.627(0)
Zn2 ×2	2.702(12)	Zn2 ×2	3.501	Zn4 ×2	2.897(15)
M ×2	2.779(6)	Zn3 − Ru1 ×2	2.530(33)	Zn2 ×4	3.219
M ×2	2.781(13)	Zn4 ×2	2.725(16)	Zn1 ×2	3.415
Ru1	3.300	M ×4	2.999(15)		
Ru2	3.325	M ×4	2.999(15)		
Ru2− Zn6	2.467(42)				
Zn4	2.616(23)				
Zn1	2.638(34)				
Zn2 ×2	2.644(6)				
Zn2 ×2	2.742(4)				
Zn5 ×2	2.755(3)				
M ×2	2.801(9)				
Ru1	3.325				

Table S6. EDX results for $Ru_{3.0}Sb_{0.97}Zn_{11.0}$ and $Ru_4Sn_{2.9}Zn_{11.6}$.

Compounds	Ru L	Sb L	Zn L
$Ru_{3.0}Sb_{0.97}Zn_{11}$			
Crystal-1	20.10	6.15	73.75
Crystal-2	20.30	6.49	73.21
Crystal-3	20.08	6.82	73.11
Crystal-4	19.72	6.66	73.62
Crystal-5	20.35	6.06	73.58
Average (100%)	20.11(4)	6.44(4)	73.45(9)
$Ru_4Sn_{2.9}Zn_{11.6}$			
Crystal-1	21.20	15.59	63.21
Crystal-2	21.18	15.37	63.45
Crystal-3	21.08	15.94	62.98
Crystal-4	21.44	15.48	63.08
Crystal-5	21.34	15.34	63.32
Average (100%)	21.25(3)	15.54(2)	63.21(3)

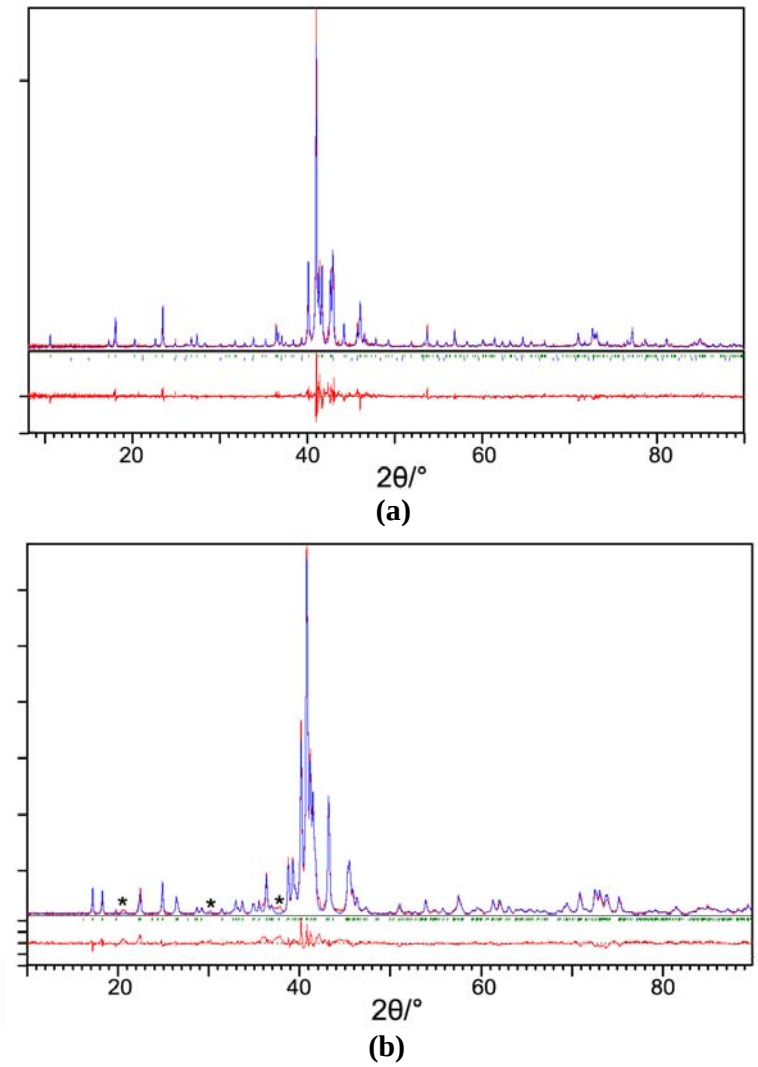
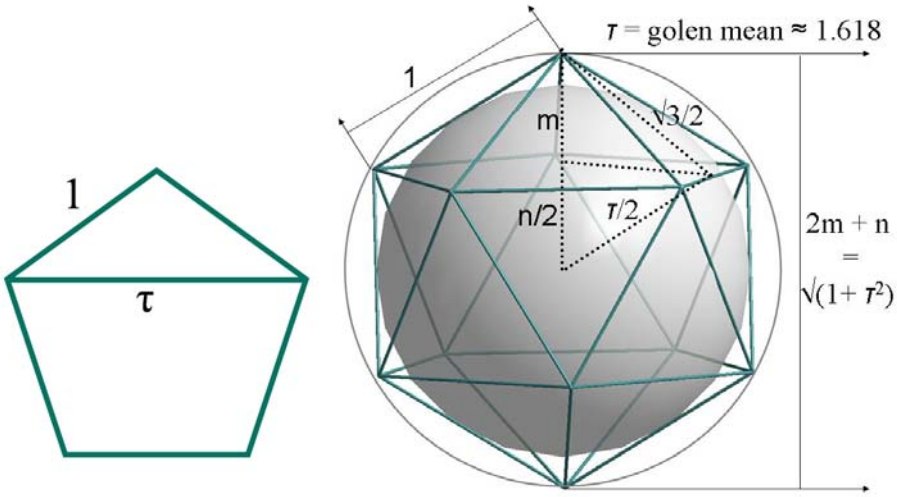
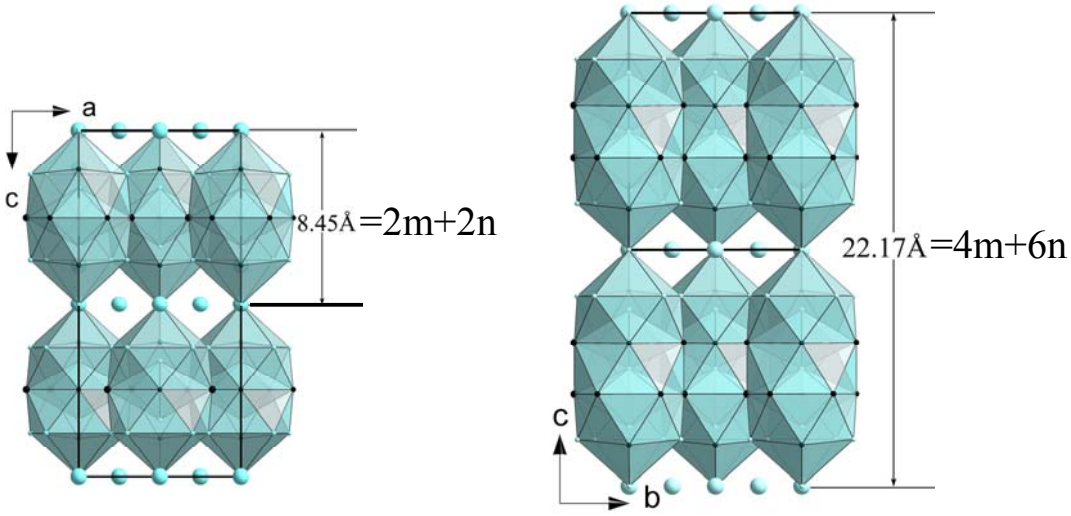


Figure S1 Rietveld refinements of and $Ru_{3.0}Sb_{0.97}Zn_{11.0}$ (a) and $Ru_4Sn_{2.9}Zn_{11.6}$ (b) shown observed and calculated powder diffraction profiles (top), difference plot of the Rietveld refinement (bottom) and the reflection positions (middle). Both phases are almost pure, except for $Ru_9Zn_7Sb_8$ (~ 3.8 wt %) as impurities in $Ru_{3.0}Sb_{0.97}Zn_{11.0}$, and unknown phase (indicated by *) in $Ru_4Sn_{2.9}Zn_{11.6}$.





$Ru_{3.0}Sb_{0.97}Zn_{11.0}$ $Ru_4Sn_{2.9}Zn_{11.6}$

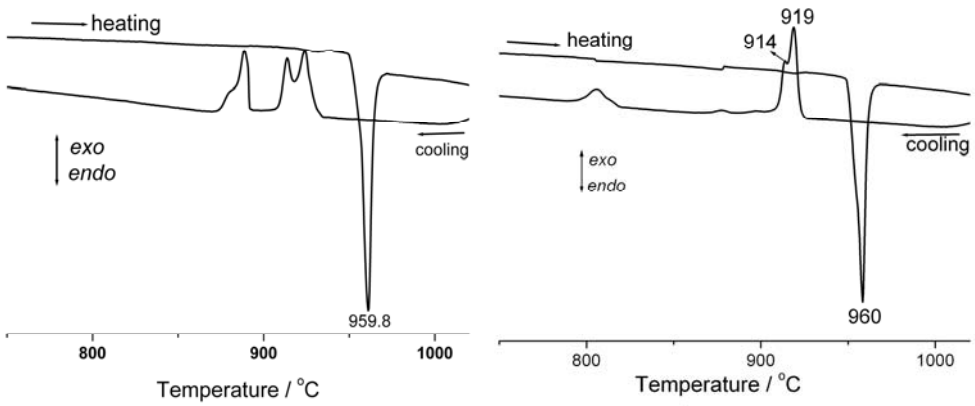
$$(\sqrt{3}/2)^2 - m^2 = (\tau/2)^2 - (n/2)^2 \quad (1)$$

$$\text{Circumdiameter} = 2m + n = \sqrt{(1+ \tau^2)} \quad (2)$$

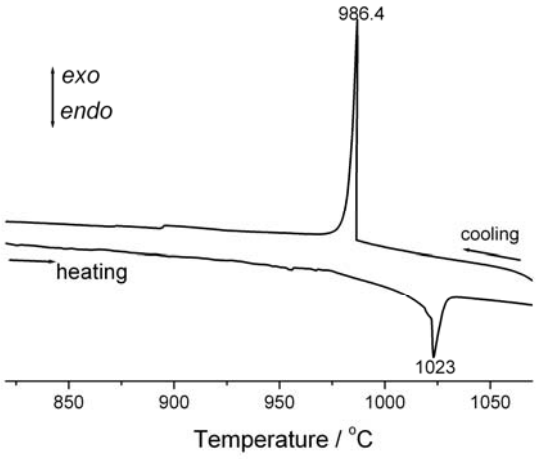
$$(4m + 6n)/(2m + 2n) = 1 + \tau = \tau^2 \quad (3)$$

$$c_{\mathbf{SbRZ}}/2 \times (1 + \tau) \approx 2c_{\mathbf{SnRZ}} \quad (4)$$

Figure S2. The relationship between the lengths of two and three interpenetrating icosahedra units. Given a regular pentagon with edge length of unity and its diagonal will be the golden mean τ. An icosahedron with edge length of unity has midradius that touches the middle of each edge equal to τ/2, and the circumdiameter equal to $\sqrt{(1+ \tau^2)}$ (Equation 2). If we denoted the length of pentagonal prism cap and antiprism in icosahedron as m and n, they can be expressed by equation (1) and (2), based on which we can present the origin of the equation (4) by equation (3). Namely, double lengths of three mutually interpenetrated icosahedra, (4m + 6n), is (1 + τ) times longer than that of two, (2m +2n).

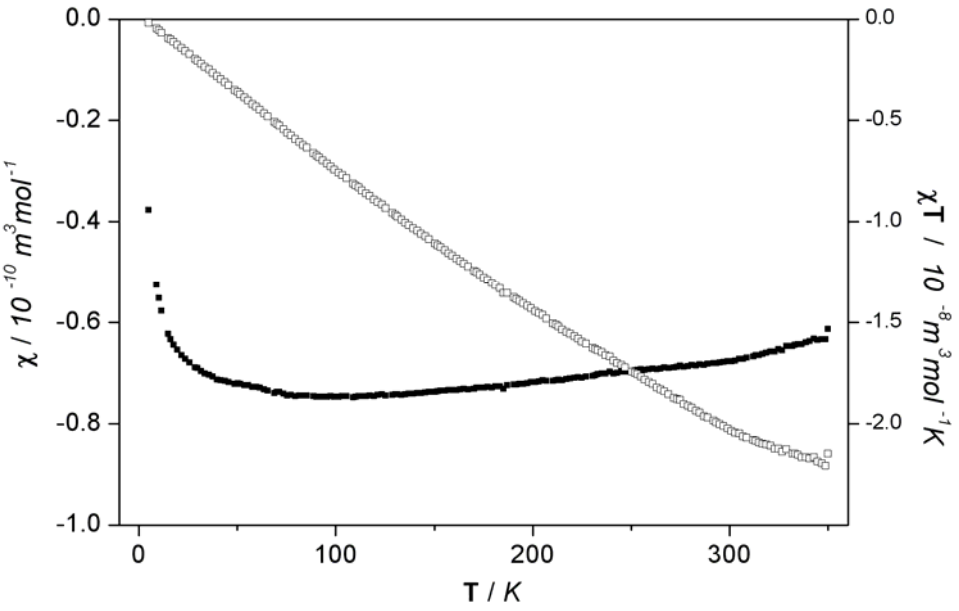


(a)

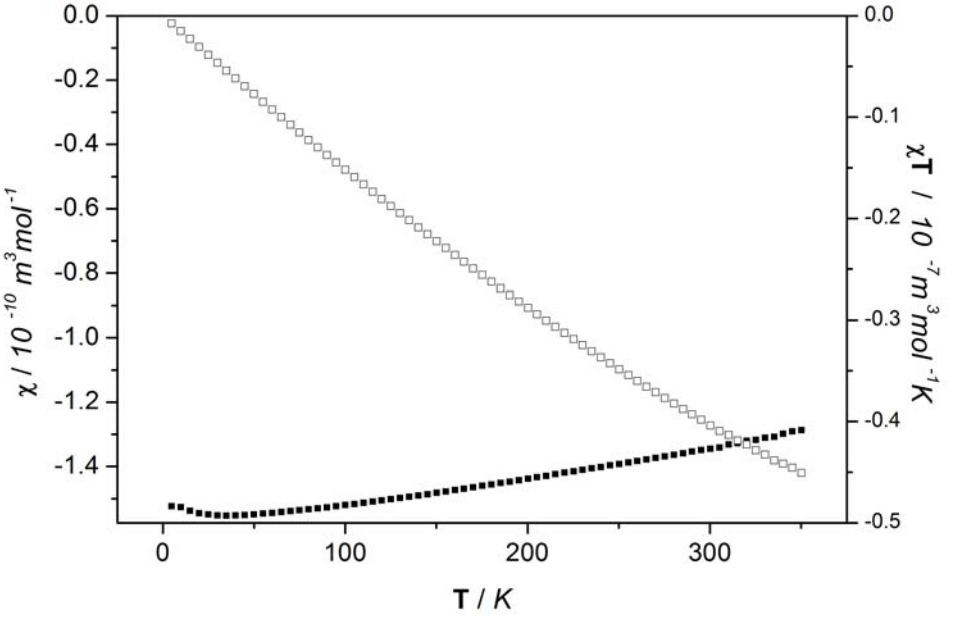


(b)

Figure S3 DTA curve for $Ru_{3.0}Sb_{0.97}Zn_{11.0}$ (a) and $Ru_4Sn_{2.9}Zn_{11.6}$ (b).



(a)



(b)

Figure S4 Temperature dependence of the magnetic susceptibilities of $Ru_{3.0}Sb_{0.97}Zn_{11.0}$ (a) and $Ru_4Sn_{2.9}Zn_{11.6}$ (b) determined with a magnetic flux of 5 Tesla.