Journal Name

Composition dependent polymorphism and superconductivity in $Y_{3+x}\{Rh,Ir\}_4Ge_{13-x}$

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Supporting Information

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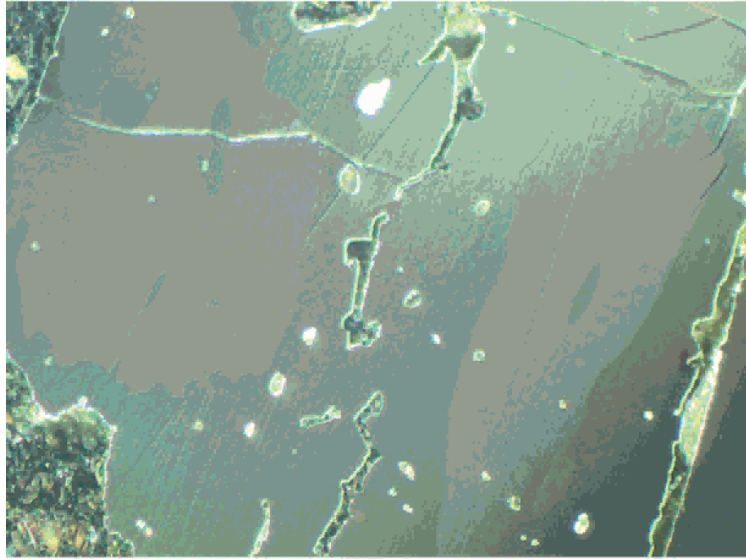
Fig. S1 The surface of the polished $Y_{3.6}Rh_4Ge_{12.4}$ sample in polarized light.
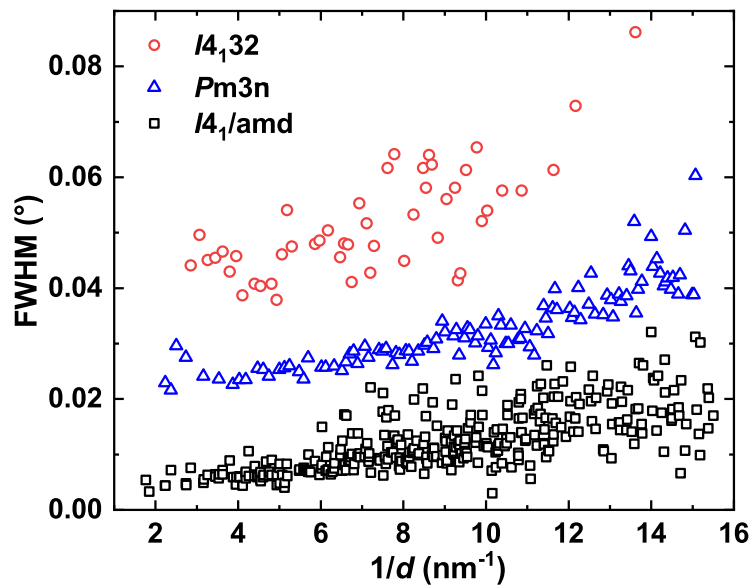

Fig. S2 Comparison of the half-widths for all three structure types within the $Y_{3+x}Rh_4Ge_{13-x}$ series. The data for the $I4_132$ and $Pm\bar{3}n$ types are analyzed in the PXRD pattern of the $x = 0.4$ sample while $I4_1/amd$ has been studied in the the $x = 0$ sample.
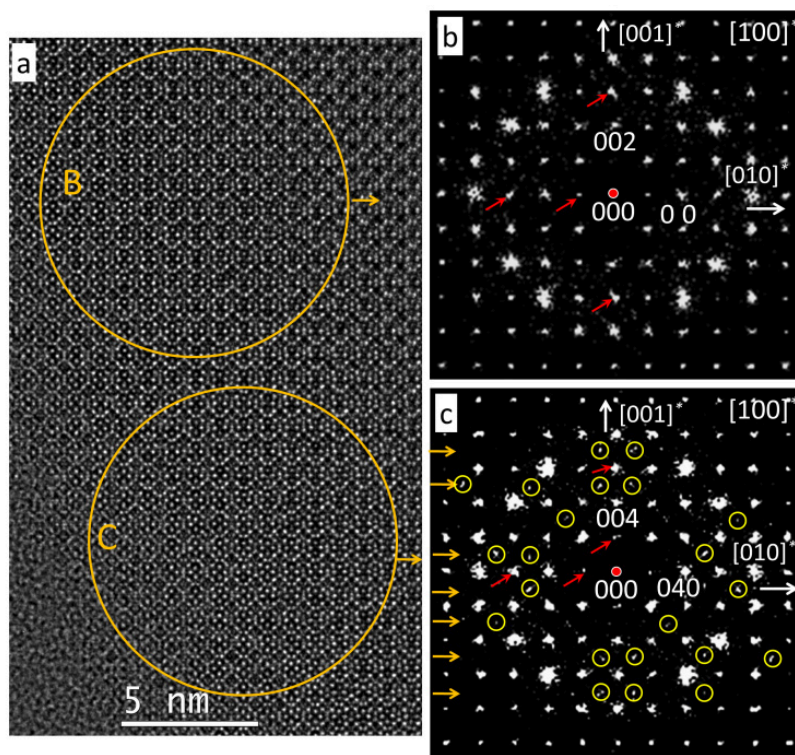
Fig. S3 (a) HR-TEM image along [100] direction of $Y_{3.6}Rh_4Ge_{12.4}$ (SG $Pm\bar{3}n$). Two regions (B and C, diameter of about 15 nm) are marked with circles and their respective FFT patterns are shown in (b) and (c). Image (b) does not show superstructure reflections and is indexed using a primitive cubic structure ($Pm\bar{3}n$). In (c) several such reflections are observed (FFT pattern indexed assuming SG $I4_132$). $Y_{3.6}Rh_4Ge_{12.4}$ is inhomogeneous at the nano-size level. This sample is thick and several forbidden reflections are observed in the FFT patterns due to dynamical multi beam effects (see red arrows).
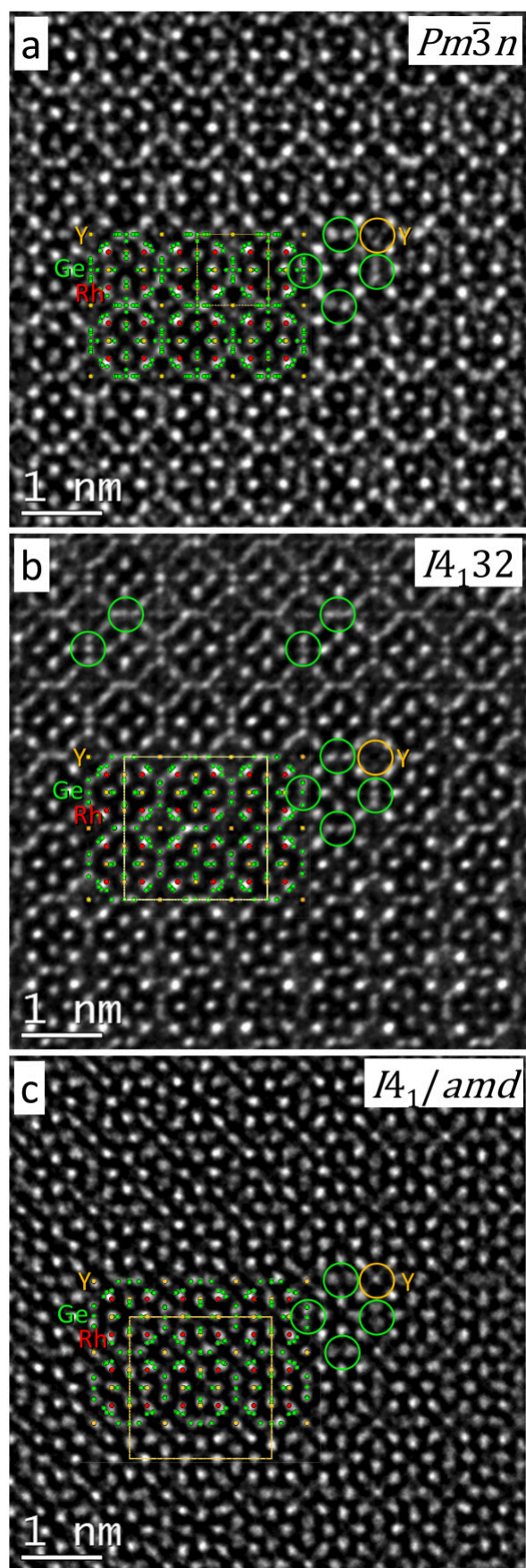
Fig. S4 HR-TEM image along [100] direction for (a) $Y_{3.6}Rh_4Ge_{12.4}$ ($Pm\bar{3}n$ type domain), (b) $Y_{3.4}Rh_4Ge_{12.6}$($I4_132$ type area) and (c) $Y_3Rh_4Ge_{13}$ ($I4_1/amd$ type). Projections of the corresponding structure models are inserted in the images. Three germanium columns (enclosed by green circles) and one Y column (yellow circle) are marked to emphasize the local differences (see also text and Fig. 6, where a more detailed view is provided).

Table S1 Atomic coordinates, occupational (G) and displacement (B) parameters for $Y_{3.6}Rh_4Ge_{12.4}$, $Y_{3.4}Rh_4Ge_{12.6}$ and $Y_{3.6}Ir_4Ge_{12.4}$.

atom	site	G^a	x/a	y/b	z/c	$B_{iso}/\text{Å}^2$
			$Y_{3.6}Rh_4Ge_{12.4}$ (SG $Pm\bar{3}n$)			
Y1	6c		1/4	0	1/2	0.46(3)
Y2	12f	0.08(2)	0.099(2)	0	0	0.7(4)
Rh	8e		1/4	1/4	1/4	0.30(2)
Ge1	2a	0.51(5)	0	0	0	0.6(1)
Ge2	24k	0.59(6)	0	0.1605(4)	0.3366(3)	0.77(5)
Ge3	24k	0.41(6)	0.1323(4)	0.2721(5)	0	0.89(7)
			$Y_{3.4}Rh_4Ge_{12.6}$ (SG $I4_132$)			
Y1	24h		0.2492(2)	$-x+1/4$	1/8	0.80(6)
Y2	24g		0.7498(2)	$x-3/4$	1/8	0.66(5)
Rh1	8b		5/8	3/8	1/8	0.7(1)
Rh2	8a		1/8	1/8	1/8	0.64(8)
Rh3	24g		0.3743(1)	1/8	$x-1/4$	0.6(1)
Rh4	24h		5/8	0.1254(2)	$-y+1/4$	0.6(1)
Ge1	16e	0.80(1)	-0.0008(2)	x	x	1.08(3)
Ge2	48i		0.5750(1)	-0.0008(3)	0.1556(1)	0.98(8)
Ge3	48i		0.6303(1)	0.0675(2)	-0.0009(3)	1.03(8)
Ge4a	48i	0.74(1)	0.1601(2)	0.0764(2)	0.0027(4)	0.69(4)
Ge4b	48i	0.26(1)	0.0002(9)	0.1192(5)	0.0665(5)	0.7(2)
T	48i	^{b}	0.5000(3)	0.1724(1)	0.0844(2)	1.15(8)
			$Y_{3.6}Ir_4Ge_{12.4}$ (SG $I4_132$)			
Y1	24h		0.2501(3)	$-x+1/4$	1/8	1.06(1)
Y2	24g		0.7506(3)	$x-3/4$	1/8	1.27(1)
Ir1	8b		5/8	3/8	1/8	0.73(1)
Ir2	8a		1/8	1/8	1/8	0.65(1)
Ir3	24g		0.3741(2)	1/8	$x-1/4$	0.97(1)
Ir4	24h		5/8	0.1252(2)	$-y+1/4$	1.05(1)
Ge1	16e		0.0018(2)	x	x	1.98(1)
Ge2	48i		0.4995(9)	0.1724(2)	0.0777(2)	1.99(1)
Ge3a	48i	0.79(1)	0.5770(2)	0.0007(9)	0.1613(2)	0.81(1)
Ge3b	48i	0.21(1)	0.5595(7)	0.000(2)	0.1189(6)	1.03(1)
Ge4a	48i	0.59(1)	0.1700(3)	0.0773(3)	0.0002(9)	0.94(1)
Ge4b	48i	0.41(1)	0.0642(4)	0.997(1)	0.3683(4)	0.81(1)
T	48i	^{c}	0.6378(2)	0.0656(2)	-0.0017(9)	1.91(3)

^{a} occupancy G is given only if it deviates from 1.0
^{b} $T = 0.94(2)\text{Ge} + 0.06(2)\text{Y}$
^{c} $T = 0.81(1)\text{Ge} + 0.19(1)\text{Y}$

Table S2 Atomic coordinates, occupational (G) and displacement (B) parameters for $Y_3Rh_4Ge_{13}$ and $Y_3Ir_4Ge_{13}$.

atom	site	G	x/a	y/b	z/c	$B_{iso}/Å^2$
			$Y_3Rh_4Ge_{13}$ (SG $I4_1/amd$)			
Y1	16g		0.2505(4)	$x+1/4$	7/8	0.47(8)
Y2	16h		0	0.1255(6)	0.0013(9)	0.55(8)
Y3	16h		0	0.1255(6)	0.4993(8)	0.47(8)
Rh1	16g		0.1256(4)	$x+1/4$	7/8	0.24(16)
Rh2	16g		0.3742(4)	$x+1/4$	7/8	0.24(16)
Rh3	32i		0.1245(4)	0.1254(4)	0.1249(2)	0.39(16)
Ge1	16h		0	0.1252(6)	0.6836(6)	0.68(4)[a]
Ge2	16h		0	0.1724(6)	0.1687(6)	0.68
Ge3	16h		0	0.0006(7)	0.2450(6)	1.34(8)
Ge4	16h		0	0.6588(6)	0.1741(6)	0.68
Ge5a	16h	0.68(3)	0	0.1597(12)	0.3237(10)	0.68
Ge5b	16h	0.32	0	0.123(3)	0.315(2)	0.68
Ge6	32i		0.2507(6)	0.1697(4)	0.1696(3)	0.68
Ge7	32i		0.3278(3)	0.0838(3)	0.5001(6)	0.68
Ge8	32i		0.0704(4)	0.0004(5)	0.1067(3)	1.34(16)
Ge9	32i		0.1358(3)	0.0667(3)	0.2500(6)	0.95(8)
			$Y_3Ir_4Ge_{13}$ (SG $I4_1/amd$)			
Y1	16g		0.2501(5)	$x+1/4$	7/8	0.92(2)
Y2	16h		0	0.1244(8)	0.0005(11)	0.92(2)
Y3	16h		0	0.1267(8)	0.4996(11)	0.92(2)
Ir1	16g		0.1251(3)	$x+1/4$	7/8	0.71(2)
Ir2	16g		0.3745(3)	$x+1/4$	7/8	0.67(2)
Ir3	32i		0.1254(3)	0.1255(3)	0.1249(2)	0.57(2)
Ge1	16h		0	0.1249(8)	0.6857(7)	1.07(2)
Ge2	16h		0	0.1723(7)	0.1695(8)	1.05(2)
Ge3	16h		0	0.0027(8)	0.2455(7)	1.29(2)
Ge4	16h		0	0.6599(8)	0.1747(8)	1.01(2)
Ge5	16h		0	0.1486(8)	0.3182(9)	1.20(2)
Ge6	32i		0.2502(8)	0.1697(5)	0.1691(4)	1.03(2)
Ge7	32i		0.3268(5)	0.0838(5)	0.5003(8)	1.01(2)
Ge8	32i		0.0683(5)	0.0007(8)	0.1084(4)	1.24(2)
Ge9	32i		0.1338(5)	0.0658(5)	0.2498(8)	1.25(2)

[a] B_{iso} for all Ge-atoms, with the exception of Ge3, Ge8, Ge9, were fixed to the same value.

Table S3 Bonding distances for all three structure types in the $Y_{3+x}Rh_4Ge_{13-x}$ system.

		$x = 0.6$ (SG $Pm\bar{3}n$)			
Y1	Ge	$3.038(2) - 3.301(4)$	Rh	Ge	$2.484(2) - 2.503(1)$
	Rh	$3.1682(1)$	Ge	Ge	$2.370(5) - 3.392(3)$
	Y1	$4.4805(1)$			
		$x = 0.4$ (SG $I4_132$)			
Y1	Ge	$3.029(5) - 3.46(1)$	Y2	Ge	$3.088(4) - 3.336(4)$
	Rh	$3.146(3) - 3.177(3)$		Rh	$3.162(3) - 3.187(4)$
	Y1	$4.4773(1)$		Y2	$4.4772(1)$
Rh1	Ge	$2.459(4)$	Rh3	Ge	$2.458(5) - 2.513(6)$
Rh2	Ge	$2.439(6) - 2.47(2)$	Rh4	Ge	$2.477(5) - 2.498(5)$
Ge	Ge	$2.464(9) - 3.454(6)$			
		$x = 0$ (SG $I4_1/amd$)			
Y1	Ge	$3.03(2) - 3.258(7)$	Y2	Ge	$3.08(2) - 3.36(2)$
	Rh	$3.15(2) - 3.17(2)$		Rh	$3.14(2) - 3.19(2)$
	Y1	$4.4775(1)$		Y2	$4.45(2) - 4.48(2)$
Y3	Ge	$3.00(2) - 3.38(2)$	Rh1	Ge	$2.46(1) - 2.495(9)$
	Rh	$3.16(2) - 3.17(2)$	Rh2	Ge	$2.469(4) - 2.51(1)$
	Y3	$4.45(2) - 4.48(2)$	Rh3	Ge	$2.46(1) - 2.52(1)$
Ge	Ge	$2.52(2) - 3.44(2)$			