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Valence fluctuations in the 3D+3 modulated $Yb_3Co_4Ge_{13}$ Remeika Phase

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Supporting Information

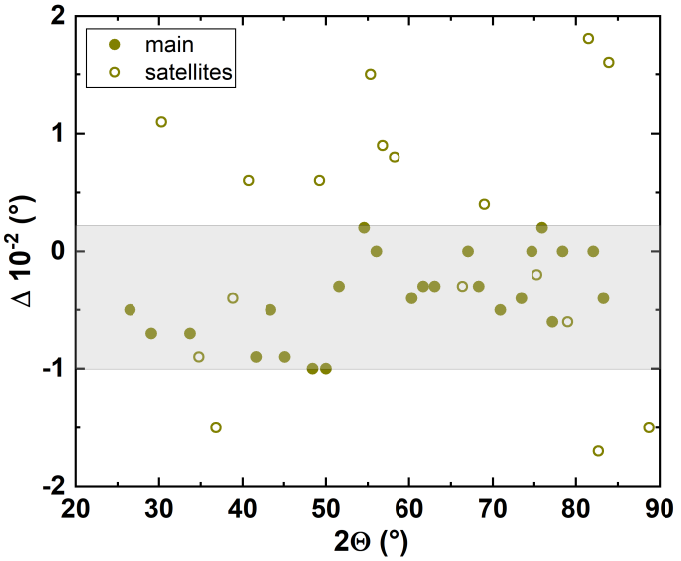

Fig. S1 Dependence of the systematic deviations Δ of reflections' indexing *vs.* 2Θ for $Yb_3Co_4Ge_{13}$.

Notes and references

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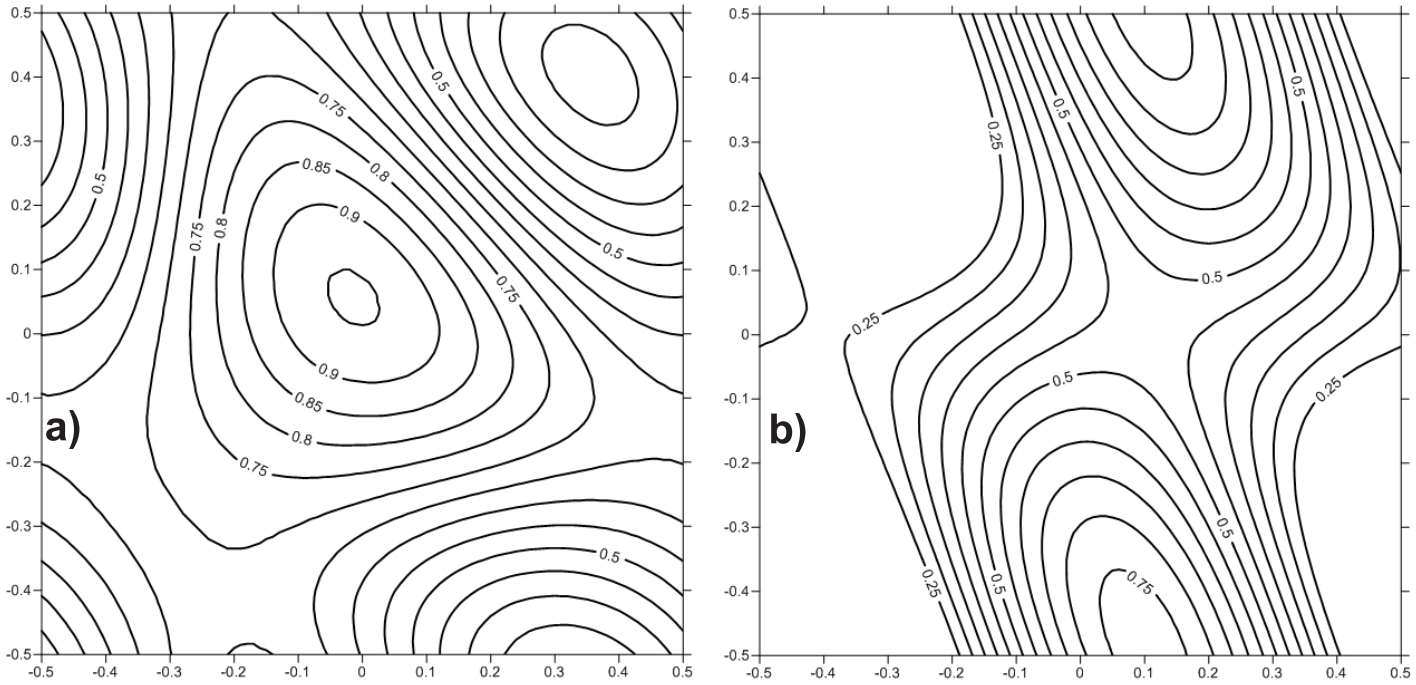

Fig. S2 2D-sections of the 3D-distributions of the occupational parameters of Ge2 (a) and Ge3 (b) atoms in the super-space on the x_6 = 0.4 level (x_4 = -0.5÷0.5; x_5 = -0.5÷0.5).

Table S1 Atomic coordinates, occupational and displacement parameters in $Yb_{3+x}Co_4Ge_{13-x}$ $(x = 0, 0.2)$

Atom	Site	G	Atomic coordinates			B_{eq}
			x	y	z	
$Yb_3Co_4Ge_{13}$ (modulated)						
Yb	6*d*	0.976(1)	0	1/4	1/2	0.690(4)
Co	8*e*		0.2488(1)	x	x	0.785(6)
Ge1	2*a*		0	0	0	0.36(1)
Ge2	24*i*	0.640(1)	0.32378(6)	0.16007(6)	0.0018(1)	0.31(1)
Ge3	24*i*	0.363(3)	0.2765(1)	0.1420(1)	0.0008(2)	0.30(4)
$Yb_3Co_4Ge_{13}$ (approximant)						
Yb1	24*g*		1/8	0.2495(9)	$y+1/4$	0.26(9)
Yb2	24*h*		1/8	0.2495(6)	$-y+1/4$	0.45(8)
Co1	8*a*		1/8	1/8	1/8	0.93(8)
Co2	8*b*		7/8	7/8	7/8	0.92(9)
Co3	24*g*		1/8	0.124(2)	$y+1/4$	0.78(9)
Co4	24*h*		1/8	0.622(2)	$-y+1/4$	0.78(5)
Ge1	16*e*		0.001(1)	x	x	0.82(5)
Ge2	48*i*		0.0881(1)	0.250(1)	0.332(2)	0.88(9)
Ge3	48*i*		0.251(1)	0.327(2)	0.407(1)	0.83(9)
Ge4	48*i*		0.001(1)	0.157(1)	0.079(2)	0.97(9)
Ge5	48*i*		0.177(2)	0.389(1)	0.251(2)	0.94(5)
$Yb_{3.2}Co_4Ge_{12.8}$						
Yb1	6*c*		1/4	0	1/2	0.51(9)
Yb2	2*a*	0.21(1)	0	0	0	0.86(8)
Co	8*e*		1/4	1/4	1/4	0.32(7)
Ge1	16*i*	0.10(1)	0.019(2)	x	x	1.0(2)
Ge2	24*k*	0.27(1)	0	0.1431(2)	0.2738(2)	0.68(2)
Ge2a	24*k*	0.73(1)	0	0.1593(2)	0.3211(2)	0.66(2)

Table S2 Modulation amplitudes of the displacive modulation in $Yb_3Co_4Ge_{13}$.

Atom	$F_{xyz}^{(i)}$	U_{cryst}	U_{powder}	Atom	$F_{xyz}^{(i)}$	U_{cryst}	U_{powder}
Yb	$F_z^{(1)}$	0.0143(1)	-0.0017(5)	Ge2	$F_x^{(23)}$	0.0110(2)	-0.0052(9)
	$F_y^{(2)}$	0.0066(1)	-0.0029(2)		$F_y^{(23)}$	-0.00136(2)	0.000(1)
	$F_{xz}^{(3)}$	0.0064(1)	-0.0003(4)		$F_z^{(23)}$	-0.0093(3)	-0.003(1)
	$F_{xz}^{(4)}$	0.0069(1)	0.0004(2)		$F_x^{(21)}$	0.0127(2)	0.0018(8)
	$F_y^{(5)}$	-0.0043(1)	0.0007(3)		$F_y^{(21)}$	0.0075(2)	0.0037(9)
	$F_{xz}^{(6)}$	0.0079(1)	-0.0016(3)		$F_z^{(21)}$	0.0108(2)	0.000(1)
	$F_y^{(7)}$	0.0097(1)	0.0039(2)		$F_x^{(24)}$	0.0064(2)	-0.0158(5)
	$F_{xz}^{(8)}$	-0.0023(2)	-0.0006(4)		$F_y^{(24)}$	0.0099(2)	-0.0068(6)
	$F_{xz}^{(9)}$	0.0074(1)	-0.0008(4)		$F_z^{(24)}$	0.0050(3)	0.0085(9)
Co	$\mathrm{F}_{\mathrm{xyz}}^{(10)}$	-0.0003(3)	-0.0004(6)	Ge3	$\mathrm{F}_{\mathrm{x}}^{(19)}$	0.0105(4)	-0.005(1)
	$F_{xyz}^{(11)}$	0.0065(2)	0.0070(5)		$F_y^{(19)}$	-0.0060(4)	0.000(1)
	$F_{xyz}^{(12)}$	-0.0139(1)	0.0023(5)		$F_z^{(19)}$	-0.0112(3)	0.002(2)
	$F_{xyz}^{(13)}$	0.0034(2)	-0.0037(8)		$F_x^{(22)}$	0.0075(3)	-0.011(1)
	$F_{xyz}^{(14)}$	0.0135(1)	-0.0036(7)		$F_y^{(22)}$	0.0238(2)	-0.001(2)
	$F_{xyz}^{(15)}$	-0.0018(2)	0.0026(8)		$F_z^{(22)}$	-0.0184(3)	-0.004(2)
Ge1	$\mathrm{F}_{\mathrm{z}}^{(16)}$	0.0106(4)	0.0172(7)		$\mathrm{F}_{\mathrm{x}}^{(20)}$	0.0146(3)	0.017(1)
	$F_{xyz}^{(17)}$	0.0171(1)	0.0021(7)		$F_y^{(20)}$	-0.0062(4)	0.004(1)
	$F_{xyz}^{(18)}$	-0.0059(2)	-0.0027(7)		$F_z^{(20)}$	0.0154(3)	0.005(2)
Ge2	$\mathrm{F}_{\mathrm{x}}^{(19)}$	-0.0055(2)	0.0029(6)		$\mathrm{F}_{\mathrm{x}}^{(23)}$	-0.0109(4)	-0.001(2)
	$F_y^{(19)}$	0.0173(2)	-0.0049(6)		$F_y^{(23)}$	0.0063(4)	0.005(2)
	$F_z^{(19)}$	0.0088(2)	-0.0044(7)		$F_z^{(23)}$	0.0057(5)	0.002(2)
	$F_x^{(22)}$	-0.0093(3)	-0.0043(9)		$F_x^{(21)}$	-0.0070(3)	-0.001(1)
	$F_y^{(22)}$	-0.0042(3)	-0.003(1)		$F_y^{(21)}$	-0.0091(3)	0.003(1)
	$F_z^{(22)}$	0.0076(3)	0.0002(8)		$F_z^{(21)}$	-0.0006(4)	0.003(2)
	$F_x^{(20)}$	0.0213(2)	-0.0069(8)		$F_x^{(24)}$	0.0198(3)	-0.0166(8)
	$F_y^{(20)}$	0.0061(2)	-0.004(1)		$F_y^{(24)}$	0.0006(4)	-0.0045(9)
	$F_z^{(20)}$	-0.0104(2)	-0.0019(9)		$F_z^{(24)}$	-0.0020(5)	-0.004(2)

Table S3 Occupational modulation amplitudes in $Yb_3Co_4Ge_{13}$.*

Atom	F_{xyz}	U_{cryst}	U_{powder}	Atom	F_{xyz}	U_{mono}	U_{Powder}
Ge2	$F^{(19)}$	0.043(3)	-0.148(7)	Ge3	$F^{(19)}$	-0.111(1)	0.167(8)
	$F^{(20)}$	-0.089(2)	-0.035(8)		$F^{(20)}$	0.006(1)	-0.007(7)
	$F^{(21)}$	-0.054(3)	0.15(1)		$F^{(21)}$	-0.260(1)	-0.14(1)
	$F^{(22)}$	0.089(3)	0.12(1)		$F^{(22)}$	-0.099(1)	-0.13(1)
	$F^{(23)}$	0.103(3)	0.04(1)		$F^{(23)}$	-0.001(1)	0.00(1)
	$F^{(24)}$	0.147(3)	0.081(6)		$F^{(24)}$	-0.007(2)	-0.146(7)

*Modulation functions for *sin* and *cos* of Fourier terms: $p = p_0 + \sum_i U^i F^i(x_4,x_5,x_6)_p$

$x = x_0 + \sum_i U^i F^i(x_4,x_5,x_6)_x$;
$y = y_0 + \sum_i U^i F^i(x_4,x_5,x_6)_y$;
$z = z_0 + \sum_i U^i F^i(x_4,x_5,x_6)_z$;

$F^{(1)} = [cos(x_5 - x_6) - cos(x_5 + x_6)]_z$
$F^{(2)} = [cos(x_4 + x_5) + cos(x_4 - x_5) - cos(x_5 - x_6) - cos(x_5 + x_6)]_y$
$F^{(3)} = [cos(x_5 + x_6) - cos(x_5 - x_6)]_x + [cos(x_4 + x_5) - cos(x_4 - x_5)]_z$
$F^{(4)} = [sin(x_4 + x_5) + sin(x_4 - x_5)]_x + [sin(x_5 + x_6) - sin(x_5 - x_6)]_z$
$F^{(5)} = [sin(x_4 + x_5) - sin(x_4 - x_5) + sin(x_5 - x_6) + sin(x_5 + x_6)]_y$
$F^{(6)} = [sin(x_5 - x_6) - sin(x_5 + x_6)]_x + [sin(x_4 + x_5) + sin(x_4 - x_5)]_z$
$F^{(7)} = [cos(x_4 + x_6) - cos(x_4 - x_6)]_y$
$F^{(8)} = [sin(x_4 + x_6)]_x - [sin(x_4 - x_6)]_z$
$F^{(9)} = [sin(x_4 - x_6)]_x + [sin(x_4 + x_6)]_z$

$F^{(10)} = [cos(x_4 + x_5)]_x + [cos(x_5 + x_6)]_y + [cos(x_4 + x_6)]_z$
$F^{(11)} = [cos(x_4 + x_6)]_x + [cos(x_4 + x_5)]_y + [cos(x_5 + x_6)]_z$
$F^{(12)} = [cos(x_5 + x_6)]_x + [cos(x_4 + x_6)]_y + [cos(x_4 + x_5)]_z$
$F^{(13)} = [sin(x_4 + x_5)]_x + [sin(x_5 + x_6)]_y + [sin(x_4 + x_6)]_z$
$F^{(14)} = [sin(x_4 + x_6)]_x + [sin(x_4 + x_5)]_y + [cos(x_5 + x_6)]_z$
$F^{(15)} = [sin(x_5 + x_6)]_x + [sin(x_4 + x_6)]_y + [sin(x_4 + x_5)]_z$

$F^{(16)} = [cos(x_4 + x_5) - cos(x_4 - x_5)]_z$
$F^{(17)} = [sin(x_4 + x_5) + sin(x_4 - x_5)]_x + [sin(x_5 + x_6) + sin(x_5 - x_6)]_y + [sin(x_4 + x_6) - sin(x_4 - x_6)]_z$
$F^{(18)} = [sin(x_4 + x_6) + sin(x_4 - x_6)]_x + [sin(x_4 + x_5) - sin(x_4 - x_5)]_y + [sin(x_5 + x_6) - sin(x_5 - x_6)]_z$

$F^{(19)} = [cos(x_4 + x_5)]$
$F^{(20)} = [cos(x_4 + x_6)]$
$F^{(21)} = [cos(x_5 + x_6)]$
$F^{(22)} = [sin(x_4 + x_5)]$
$F^{(23)} = [sin(x_4 + x_6)]$
$F^{(24)} = [sin(x_5 + x_6)]$

Table S4 Anisotropic parameters for the modulated $Yb_3Co_4Ge_{13}$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Yb	0.532(6)	1.01(1)	B11	0	0	0
Co	0.79(1)	B11	B11	0.140(6)	B12	B12
Ge1	0.36(2)	B11	B11	0	0	0
Ge2	0.17(2)	0.15(2)	0.61(2)	0.022(8)	0.02(2)	0.02(2)
Ge3	0.44(7)	0.25(6)	0.21(6)	0.07(3)	-0.18(4)	0.15(4)

Table S5 Interatomic distances (Å) in $Yb_{3+x}Co_4Ge_{13-x}$ ($x = 0, 0.2$)

Contact	$Yb_3Co_4Ge_{13}$ ($I4_132$)	$Yb_{3.2}Co_4Ge_{12.8}$ ($Pm\bar{3}n$)
Yb-Ge	$2.990(2) - 3.186(3)$	$3.026(1) - 3.201(1)$
Yb-Co	$3.047(3) - 3.170(3)$	$3.0903(1) - 3.7848(1)$
Yb-Yb	$4.3613(1)$	$4.3704(1)$
Co-Ge	$2.355(4) - 2.430(4)$	$2.3856(6) - 3.499(2)$
Co-Co		> 4.3 Å
Ge-Ge	$2.630(2) - 3.412(4)$	$2.484(2) - 3.359(2)$