Supporting Information

For

Synthesis, Structure, and Bonding in $K_{12}Au_{21}Sn_4$ – A Polar Intermetallic Compound with Dense Au_{20} and open $AuSn_4$ Layers

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Table S1 Detailed Crystallographic Data for $K_{12}Au_{21}Sn_4$

Empirical formula	**$K_{12}Au_{21}Sn_4$**
fw / g·mol^{-1}	5080.26
space group, *Z*	*Pmmn* (No.59, Origin 2), 2
unit cell parameters	*a* = 12.162(2) Å
	b = 18.058(4) Å
	c = 8.657(2) Å
	V = 1901.3(7) Å^3
ρ_{calc} / g·cm^{-3}	8.87
μ / mm^{-1} (Mo Kα)	84.5
crystal size / mm^3	0.09 × 0.12 × 0.16
Diffractometer	Bruker Apex (CCD)
absorption correction	numerical (X-shape)
Reflections collected	20794 (R_{int} = 0.224)
obs. data / restr. / para.	2398 / 0 / 103
goodness-of-fit on F^2	0.935
R_1 / wR_2 [$I > 2\sigma(I)$]	0.047 / 0.105
R_1 / wR_2 (all data)	0.074 / 0.115
largest diff. peak and hole / e·Å^{-3}	+5.50 [1.04 Å from Au3]
	−3.28 [0.88 Å from Au4]

Table S2 Interatomic Distances $K_{12}Au_{21}Sn_4$ (≤ 4Å)

Atom pair	**Distance**	**Atom pair**	**Distance**	**Atom pair**	**Distance**
Au1–Au3	2.778(2)	Au2–K4	3.582(5)	Au7–K5	3.744(4)
Au1–Au4	2.791(2)	Au2–K1	3.850(5)	Au8–K3	3.865(7)
Au1–Au2	2.817(1)	Au2–K1	3.862(5)	Sn1–K1	3.555(5)
Au1–Au1	2.914(2)	Au3–K3	3.285(7)	Sn1–K3	3.930(7)
Au2–Au5	2.774(1)	Au3–K1	3.477(5)	Sn1–K5	3.661(8)
Au2–Au7	2.784(1)	Au3–K2	3.550(8)	Sn1–K4	3.977(7)
Au2–Au2	2.785(2)	Au3–K1	3.599(5)	Sn2–K5	3.749(9)
Au2–Au3	2.794(1)	Au4–K4	3.221(7)	Sn2–K3	3.865(6)
Au2–Au6	2.837(1)	Au4–K1	3.477(5)	Sn2–K1	3.501(5)
Au3–Sn1	2.643(2)	Au4–K2	3.799(7)	Au8–K4	3.778(8)
Au4–Sn2	2.634(2)	Au4–K6	3.66(1)	Sn2–K4	3.896(8)
Au4–Au4	2.729(2)	Au5–K4	3.271(3)	Au1–K4	3.474(7)
Au5–Sn1	2.620(2)	Au5–K2	3.510(7)	Au1–K6	3.62(1)
Au5–Au2	2.774(1)	Au5–K3	3.632(6)	Au1–K1	3.715(5)
Au5–Au6	2.775(1)	Au5–K5	3.695(3)	Au1–K2	3.920(8)
Au5–Au7	2.783(1)	Au6–K3	3.578(4)	K1–K1	3.399(9)
Au6–Au7	2.746(1)	Au6–K2	3.642(4)	K1–K2	3.516(7)
Au7–Sn2	2.611(2)	Au6–K1	3.713(5)	K2–K6	3.664(9)
Au8–Sn2	2.800(2)	Au7–K3	3.393(3)	K3–K5	3.579(9)
Au8–Sn1	2.805(2)	Au7–K1	3.456(5)	K3–K2	3.86(1)
Au2–K3	3.474(6)	Au7–K6	3.538(2)	K4–K5	3.564(9)
Au2–K2	3.500(7)	Au7–K4	3.548(7)	Au5–K1	3.437(5)
Au2–K6	3.552(4)	Au7–K2	3.553(4)		

Table S3 Anisotropic displacement parameters ($Å^2 \times 10^3$) for $K_{12}Au_{21}Sn_4$

Atom	U_{11}	U_{22}	U_{33}	**Atom**	U_{11}	U_{22}	U_{33}
Au1	14(1)	15(1)	24(1)	Sn1	8(1)	16(1)	16(1)
Au2	9(1)	19(1)	17(1)	Sn2	12(1)	13(1)	18(1)
Au3	14(1)	15(1)	18(1)	K1	19(2)	24(3)	21(2)
Au4	11(1)	25(1)	21(1)	K2	23(4)	38(5)	23(4)
Au5	12(1)	20(1)	18(1)	K3	13(3)	26(4)	27(4)
Au6	14(1)	18(1)	19(1)	K4	20(3)	24(4)	32(4)
Au7	16(1)	23(1)	18(1)	K5	24(6)	26(5)	29(5)
Au8	22(1)	21(1)	28(1)	K6	29(6)	21(5)	29(5)

Table S4 Integrated DOS Values for 6*s*, 6*p*, and their Ratio for the Different Au Atoms in $K_{12}Au_{21}Sn_4$

Au atom (*Wyck.*)	**$IDOS_{6s}$**	**$IDOS_{6p}$**	**$IDOS_{5d}$**	**$IDOS_{5p}/IDOS_{5s}$**
4*b*-Au8 (2*b*)	2.09	2.06	18.90	0.99
6*b*-Au1 (4*e*)	4.06	2.74	37.72	0.67
6*b*-Au2 (8*g*)	7.89	5.16	74.88	0.65
6*b*-Au6 (4*c*)	4.26	3.28	37.94	0.77
exo*b* Au3 (4*e*)	3.91	2.04	36.80	0.52
exo*b* Au4 (4*f*)	3.91	2.22	36.67	0.57
exo*b* Au5 (8*g*)	7.84	4.05	73.08	0.52
exo*b* Au7 (8*g*)	7.75	3.98	73.02	0.51

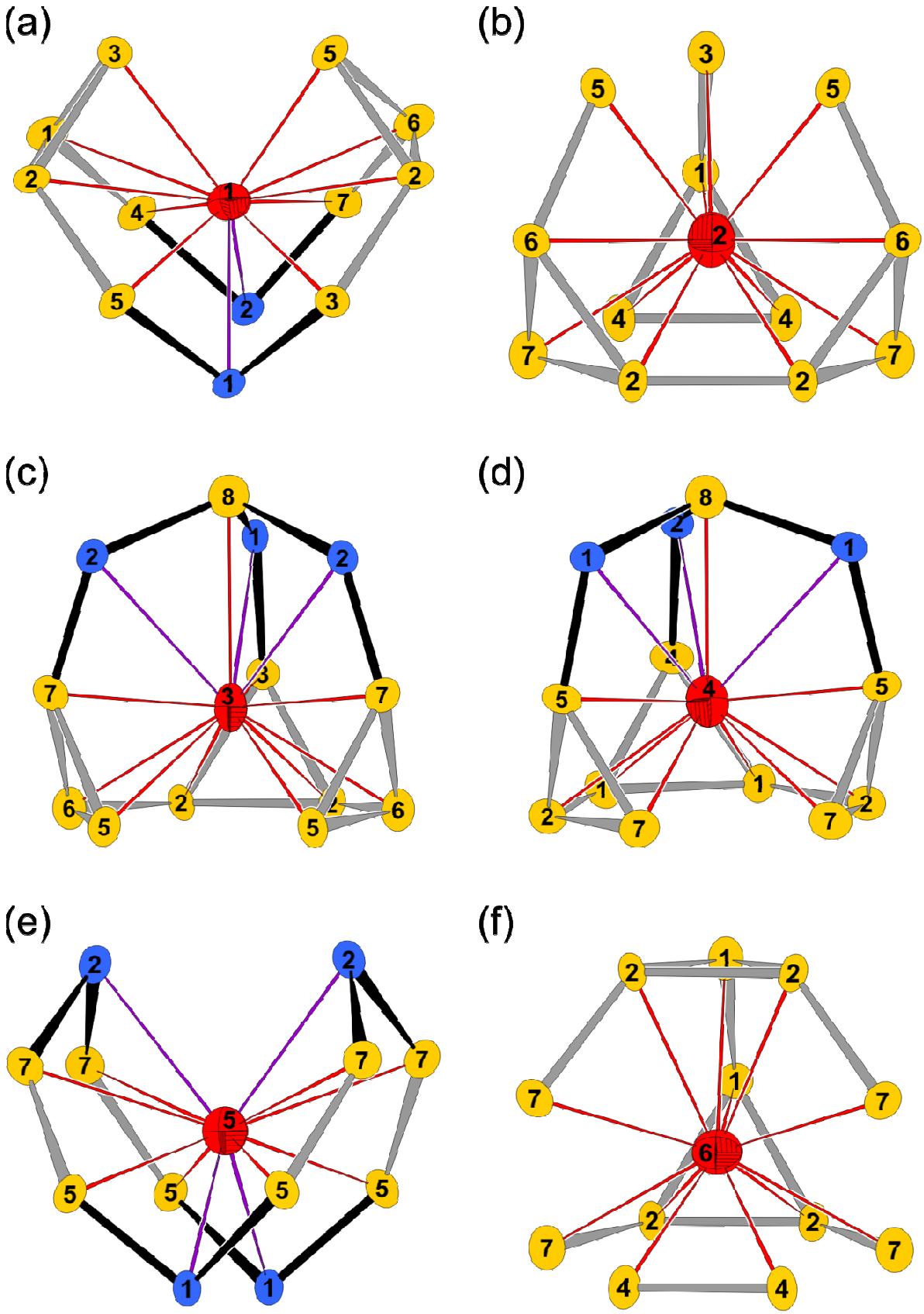

Figure S1 (a–f) Next nearest Au and Sn neighbors of the different K atoms in $K_{12}Au_{21}Sn_4$. The cut–off value is 4 Å (95% ellipsoids).

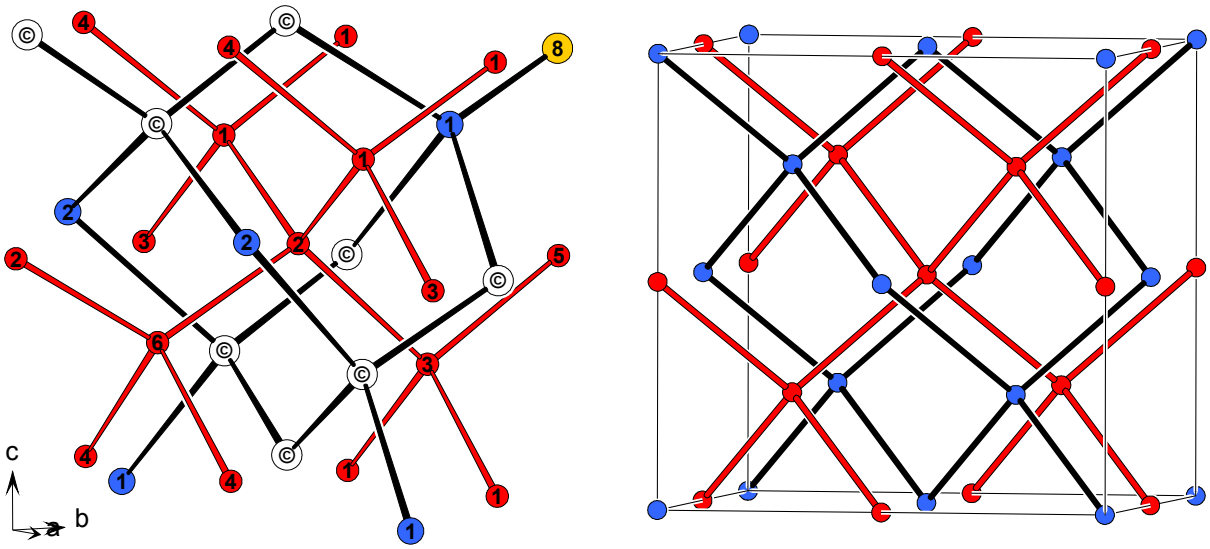

Figure S2 Left: The structure of $K_{12}Au_{21}Sn_4$ as a pseudo-NaTl derivative with Au_4 network centers '©' plus Sn (blue) centers and cation positions (red) connected separately. Right: Unit cell of NaTl.

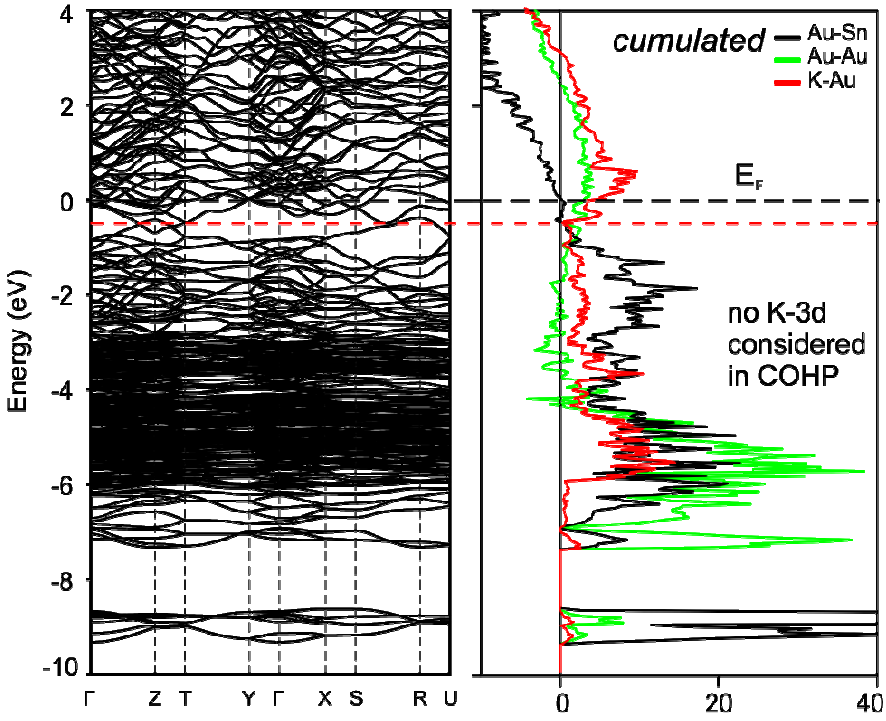

Figure S3 (a) Band dispersion and (b) cumulative −COHP diagram with K 3*d* omitted.

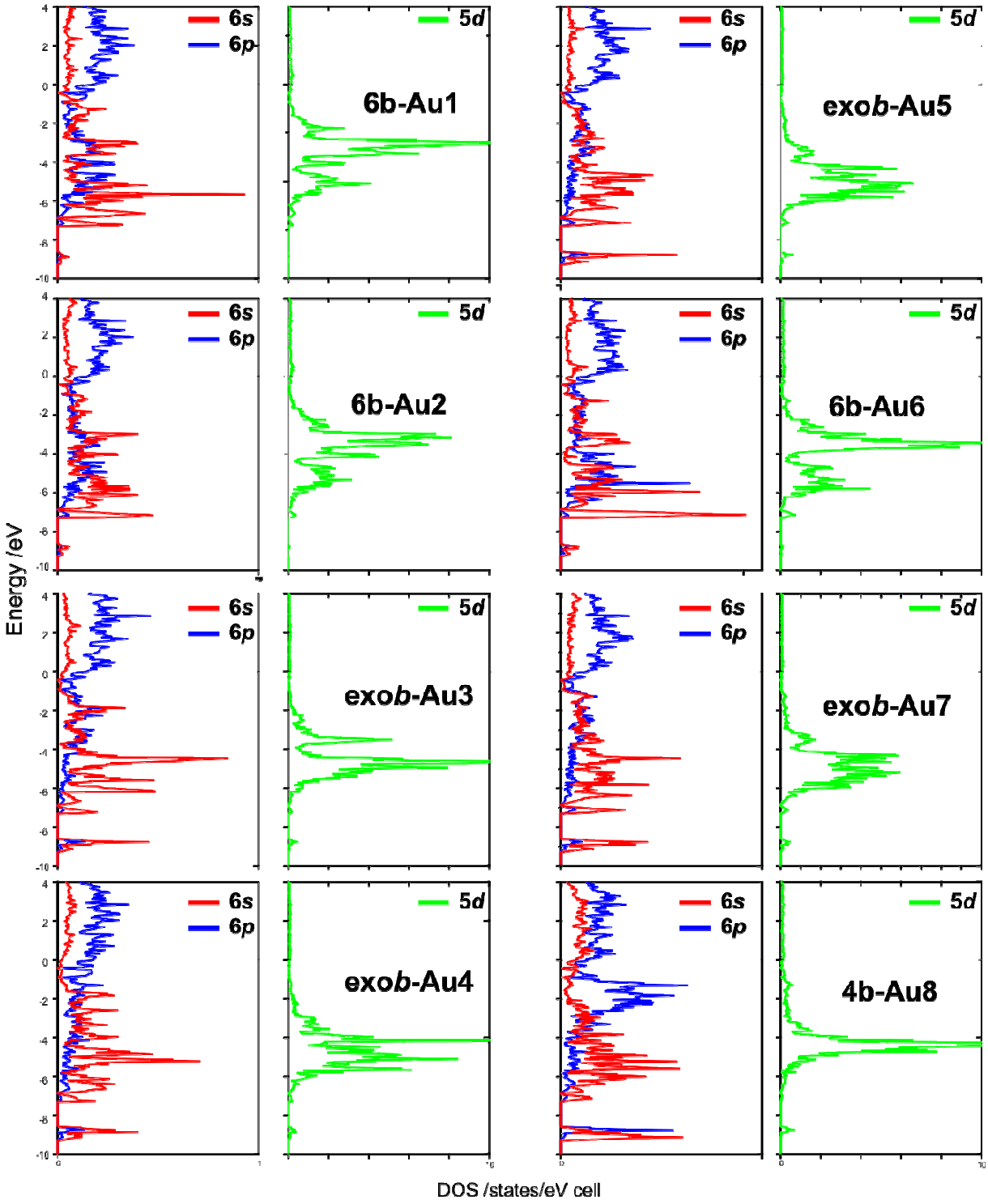

Figure S4 Orbital contributions to the DOS for the different Au atoms in $K_{12}Au_{21}Sn_4$, all on a per-atom basis.

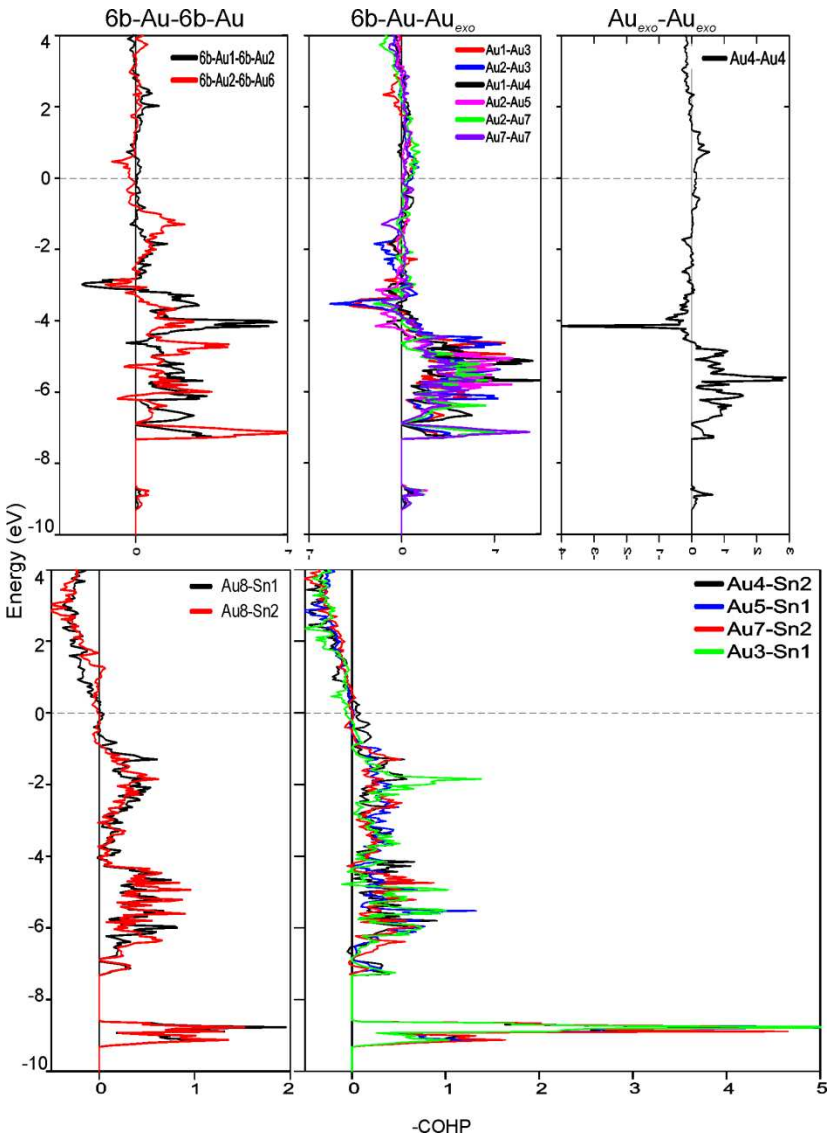

Figure S5 Individual Au–Au and Au–Sn −COHP diagrams for $K_{12}Au_{21}Sn_4$.