Supporting Information

for

Na_6ZnSn_2, $Na_{4.24}K_{1.76(1)}ZnSn_2$, and $Na_{20}Zn_8Sn_{11}$: Three Intermetallic Structures Containing the Linear $\{Sn–Zn–Sn\}^{6-}$ Unit

Sung-Jin Kim, Florian Kraus, Thomas F. Fässler*

Table S1. Atomic coordinates and equivalent displacement parameters for Na_6ZnSn_2, $Na_{4.24}K_{1.76(1)}ZnSn_2$, and $Na_{20}Zn_8Sn_{11}$.

Atom	Wyck.	Occ. ≠ 1	*x*	*y*	*z*	U_{eq} / Å^2
			Na_6ZnSn_2 (1)			
Sn	4*i*		0.1447(1)	0	0.2490(1)	0.031(1)
Zn	2*a*		0	0	0	0.037(1)
Na1	4*i*		0.4703(2)	0	0.2753(3)	0.053(1)
Na2	4*i*		0.2926(3)	0	0.9295(3)	0.055(1)
Na3	4*i*		0.1736(2)	0	0.5908(3)	0.056(1)
			$Na_{4.24}K_{1.76(1)}ZnSn_2$ (2)			
Sn1	4*e*		0.3397(3)	0.7238(3)	0.0788(1)	0.033(1)
Sn2	4*e*		0.1485(1)	0.1922(1)	0.8852(1)	0.036(1)
Zn	4*e*		0.2565(1)	0.9648(1)	0.9885(1)	0.038(2)
A = K1 / Na1	4*e*	0.77/ 0.23(1)	0.3243(1)	0.3913(1)	0.2036(1)	0.047(5)
K2	4*e*		0.6447(1)	0.5333(1)	0.1828(1)	0.052(3)
Na2	4*e*		0.5072(2)	0.8222(2)	0.9263(2)	0.050(5)
Na3	4*e*		0.1683(2)	0.7224(2)	0.2380(2)	0.048(5)
Na4	4*e*		0.0766(2)	0.5241(2)	0.8787(2)	0.053(5)
Na5	4*e*		0.0112(2)	0.3404(3)	0.5769(2)	0.055(6)
			$Na_{20}Zn_8Sn_{11}$ (3)			
Sn1	8*f*		0.1844(1)	0.2199(1)	0.2932(1)	0.017(1)
Sn2	8*f*		0.1351(1)	–0.2843(1)	0.3308(1)	0.018(1)
Sn3	8*f*		–0.0238(1)	–0.4429(1)	0.3311(1)	0.016(1)
Sn4	8*f*		–0.0477(1)	0.0351(1)	0.4065(1)	0.024(1)
Sn5	8*f*		0.3241(1)	0.0137(1)	0.4892(1)	0.027(1)
M = Sn / Zn	8*f*	0.50 / 0.50	0.0873(1)	–0.0402(1)	0.2655(1)	0.020(1)
Zn1	8*f*		–0.0237(1)	–0.1322(1)	0.3314(1)	0.021(1)
Zn2	8*f*		0.0870(1)	0.4697(1)	0.2680(1)	0.018(1)
Zn3	8*f*		0.3441(1)	0.2133(1)	0.2694(1)	0.019(1)
Zn4	4*d*		¼	¼	½	0.077(1)
Na1	8*f*		0.0145(3)	0.2141(4)	0.1873(2)	0.028(1)
Na2	8*f*		0.2067(2)	0.0228(4)	0.1880(2)	0.027(1)
Na3	8*f*		0.1570(3)	0.0256(5)	0.3936(2)	0.032(1)
Na4	8*f*		0.2058(3)	0.4039(5)	0.1881(2)	0.037(1)
Na5	8*f*		0.1564(3)	0.4021(5)	0.3935(2)	0.038(1)
Na6	8*f*		0.3470(3)	0.2156(5)	0.3937(2)	0.032(1)
Na7	8*f*		0.0657(3)	–0.2681(5)	0.4399(2)	0.040(1)
Na8	8*f*		–0.0240(3)	–0.6179(5)	0.4392(2)	0.041(1)
Na9	8*f*		0.2863(3)	–0.3098(5)	0.4397(2)	0.041(1)
Na10	8*f*		0.0823(5)	0.0852(7)	0.4998(2)	0.087(3)

Table S2. Anisotropic displacement parameters (/ Å^2) for Na_6ZnSn_2, $Na_{4.24}K_{1.76(1)}ZnSn_2$, and $Na_{20}Zn_8Sn_{11}$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			Na_6ZnSn_2 (1)			
Sn	0.034(1)	0.027(1)	0.032(1)	0	0.004(1)	0
Zn	0.033(1)	0.037(1)	0.039(1)	0	–0.003(1)	0
Na1	0.041(1)	0.043(1)	0.077(2)	0	0.015(1)	0
Na2	0.078(1)	0.034(1)	0.059(1)	0	0.034(1)	0
Na3	0.067(1)	0.050(1)	0.050(1)	0	0	0
			$Na_{4.24}K_{1.76(1)}ZnSn_2$ (2)			
Sn1	0.034(1)	0.035(1)	0.032(1)	0.004(1)	0.017(1)	0.003(1)
Sn2	0.033(1)	0.039(1)	0.035(1)	0.006(1)	0.016(1)	0.006(1)
Zn	0.040(1)	0.031(1)	0.039(1)	0	0.017(1)	0
A = K1 / Na1	0.054(1)	0.043(1)	0.048(1)	0.005(1)	0.028(1)	0
K2	0.053(1)	0.049(1)	0.055(1)	0.006(1)	0.028(1)	0.008(1)
Na2	0.044(1)	0.058(1)	0.046(1)	0	0.022(1)	–0.007(1)
Na3	0.040(1)	0.063(1)	0.040(1)	0	0.020(1)	0.004(1)
Na4	0.055(1)	0.049(1)	0.056(1)	0	0.028(1)	0
Na5	0.050(1)	0.072(2)	0.043(1)	0.003(1)	0.023(1)	0.004(1)
			$Na_{20}Zn_8Sn_{11}$ (3)			
Sn1	0.014(1)	0.013(1)	0.024(1)	0	0.005(1)	0
Sn2	0.015(1)	0.016(1)	0.024(1)	–0.003(1)	0.005(1)	–0.002(1)
Sn3	0.015(1)	0.013(1)	0.020(1)	0	0.004(1)	0
Sn4	0.026(1)	0.021(1)	0.025(1)	–0.003(1)	0.008(1)	0
Sn5	0.033(1)	0.023(1)	0.024(1)	0	0.005(1)	0.008(1)
M = Sn / Zn	0.021(1)	0.013(1)	0.026(1)	0	0.006(1)	0
Zn1	0.022(1)	0.016(1)	0.024(1)	–0.002(1)	0.006(1)	0
Zn2	0.018(1)	0.015(1)	0.021(1)	0	0.004(1)	0
Zn3	0.017(1)	0.017(1)	0.023(1)	0.002(1)	0.005(1)	0.002(1)
Zn4	0.131(3)	0.059(2)	0.039(1)	0.002(1)	0.013(1)	0.062(1)
Na1	0.032(2)	0.019(2)	0.033(2)	–0.004(2)	0.009(2)	0
Na2	0.021(2)	0.027(2)	0.034(2)	0	0.006(2)	–0.004(2)
Na3	0.032(2)	0.030(2)	0.034(2)	0	0.006(2)	–0.004(2)
Na4	0.023(2)	0.033(2)	0.057(3)	0.004(2)	0.012(2)	0.007(2)
Na5	0.045(2)	0.040(3)	0.029(2)	–0.003(2)	0.005(2)	0.012(2)
Na6	0.030(2)	0.033(2)	0.033(2)	0.003(2)	0.011(2)	0
Na7	0.046(3)	0.039(3)	0.033(2)	0.006(2)	0.004(2)	0.012(2)
Na8	0.046(3)	0.032(2)	0.048(3)	0	0.020(2)	0
Na9	0.032(2)	0.043(3)	0.046(3)	–0.009(2)	0.006(2)	0
Na10	0.176(7)	0.075(4)	0.002(2)	0	0.004(3)	0.085(5)

Table S3. Interatomic distances (≤ 4 Å) in Na_6ZnSn_2, $Na_{4.24}K_{1.76(1)}ZnSn_2$, and $Na_{20}Zn_8Sn_{11}$. (standard deviation of the last digit in parentheses). A = Na1 / K1, M = Sn / Zn.

Atom pair		*d* / Å	Atom pair		*d* / Å	Atom pair		*d* / Å
				Na_6ZnSn_2 (1)				
Sn	Zn	2.561(1)	Na1	Sn	3.255(2)	Na2	Zn	3.450(2)×2
	Na3	3.157(3)		Na2	3.260(3)		Na1	3.459(4)
	Na1	3.255(2)		Sn	3.280(1)×2		Sn	3.511(2)
	Na1	3.280(1)×2		Na3	3.414(2)×2	Na3	Sn	3.157(3)
	Na2	3.309(1)×2		Na2	3.459(4)		Na2	3.214(4)
	Na3	3.507(2)×2		Na3	3.630(3)		Na1	3.414(2)×2
	Na2	3.511(2)	Na2	Zn	3.110(2)		Sn	3.507(2)×2
	Na3	3.723(3)		Na2	3.205(2)×2		Na1	3.630(3)
Zn	Sn	2.561(1)×2		Na3	3.214(4)		Na3	3.667(5)×3
	Na2	3.110(2)×2		Na1	3.260(3)		Sn	3.723(3)
	Na2	3.450(2)×4		Sn	3.309(1)×2			
				$Na_{4.24}K_{1.76(1)}ZnSn_2$ (2)				
Sn1	Zn	2.582(1)	A	Na2	3.640(2)	Na4	Sn2	3.300(2)
	Na3	3.280(2)		Na2	3.692(3)		Sn2	3.369(2)
	Na2	3.317(2)		K2	3.717(2)		Na5	3.394(3)
	Na4	3.397(2)		Sn2	3.728(1)		Sn1	3.397(2)
	Na3	3.422(2)		Na2	3.737(2)		Na3	3.406(3)
	Na2	3.478(2)		Sn1	3.814(2)		Na3	3.466(3)
	A	3.612(1)		Na3	3.843(2)		Na5	3.620(3)
	K2	3.646(1)		Na5	3.913(3)		A	3.636(3)×2
Sn1	Na5	3.729(2)	A	Zn	3.955(1)	Na4	K2	3.664(3)
	A	3.814(1)	Na2	Zn	3.199(2)		Na4	3.973(4)
	K2	3.981(1)		Sn1	3.317(2)		Na3	4.176(3)
Sn2	Zn	2.556(1)		Na3	3.454(3)	Na5	Zn	3.065(2)
	Na5	3.285(2)		Sn1	3.478(2)		Sn2	3.285(2)
	Na4	3.300(2)		Sn2	3.482(2)		Na3	3.352(3)
	Na3	3.328(2)		Zn	3.593(2)		Sn2	3.393(2)
	Na4	3.369(2)		A	3.640(2)×2		Na4	3.394(3)
	Na5	3.393(2)		A	3.692(3)×2		Na5	3.549(5)
	Na2	3.482(2)		A	3.737(2)×2		Na4	3.620(3)
	A	3.634(1)×2	Na3	Zn	3.117(2)		Na3	3.661(3)
	A	3.728(1)×2		Sn1	3.280(2)		Sn1	3.729(2)
	K2	3.933(1)		Sn2	3.328(2)	K2	Zn	3.401(1)
Zn	Sn2	2.556(1)		Na5	3.352(3)		Na3	3.604(3)
	Sn1	2.582(1)		Na4	3.406(3)		Sn1	3.646(1)
	Na5	3.065(2)		Sn1	3.422(2)		Na4	3.664(3)
	Na3	3.117(2)		Na2	3.454(3)		A	3.717(2)×2
	Na2	3.199(2)		Na4	3.466(3)		Na5	3.771(3)
	K2	3.401(1)		K2	3.604(3)		Na2	3.824(2)
	Na2	3.593(2)		Na5	3.661(3)		Na2	3.845(3)
	A	3.955(1)		A	3.843(2)		K2	3.912(3)
A	Sn1	3.612(1)		K2	3.771(3)		Sn2	3.933(1)
	Sn2	3.634(1)		A	3.913(3)×2		Sn1	3.981(1)
	Na4	3.636(3)						

Atom pair		*d* / Å	Atom pair		*d* / Å	Atom pair		*d* / Å
				$Na_{20}Zn_8Sn_{11}$ (3)				
Sn1	Zn2	2.799(1)	Zn1	Sn4	2.687(1)	Na3	Sn5	3.327(4)
	Zn3	2.802(1)		M	2.774(1)×2		Sn2	3.333(4)
	M	2.886(1)		Zn3	2.811(2)		Zn1	3.370(4)
	Na2	3.294(4)		Sn3	2.882(1)		Sn4	3.406(4)
	Na5	3.360(4)		Sn2	2.930(1)		Sn1	3.415(4)
	Na6	3.365(4)		M	2.952(1)		Na10	3.457(7)
	Na1	3.375(4)		Na2	3.222(4)		Na7	3.475(6)
	Na4	3.405(5)		Na1	3.263(4)		Na5	3.492(6)
	Na3	3.415(4)		Na7	3.270(5)		M	3.514(4)
	Na4	3.449(5)		Na6	3.305(4)		Na6	3.538(6)
	Na2	3.516(4)	Zn2	Zn2	2.763(2)		Na1	3.597(6)
Sn2	Zn3	2.860(1)		Sn1	2.799(1)	Na4	Sn3	3.200(4)
	Zn2	2.866(1)		Sn3	2.815(1)		Sn2	3.245(4)
	M	2.890(1)		Zn3	2.815(2)		Zn3	3.269(5)
	Zn1	2.930(1)		Sn2	2.866(1)		Zn2	3.289(4)
	Sn3	2.959(1)		Sn3	2.878(1		Zn3	3.302(4)
	Na4	3.245(4)		Na1	3.276(4)		M	3.341(4)×2
	Na2	3.256(4)		Na1	3.283(4)		Sn1	3.405(5)
	Na3	3.333(4)		Na4	3.289(5)		Sn1	3.449(5)
	Na5	3.363(5)		Na2	3.317(4)		Na2	3.535(6)
	Na9	3.427(5)		Na5	3.450(4)		Na1	3.551(6)
	Na7	3.442(5)	Zn3	Sn1	2.802(1)		Na2	3.568(6)
Sn3	Zn3	2.813(1)		M	2.804(1)×2	Na5	Sn5	3.274(4)
	Zn2	2.815(1)		Zn1	2.811(2)		Zn4	3.303(4)
	Zn2	2.878(1)		Sn3	2.813(1)		Sn3	3.356(4)
	Zn1	2.882(1)		Zn2	2.815(2)		Sn1	3.360(4)
	Sn2	2.959(1)		Sn2	2.860(1)		Sn2	3.363(5)
	Na4	3.200(4)		Na4	3.269(5)		Na8	3.429(6)
	Na1	3.231(4)		Na2	3.276(4)		Zn2	3.450(4)
	Na6	3.335(4)		Na2	3.294(4)		Na9	3.459(7)
	Na5	3.356(4)		Na4	3.302(4)		Na3	3.492(6)
Sn3	Na8	3.398(5)	Zn3	Na6	3.421(4)	Na5	Na6	3.530(6)
	Na7	3.433(5)	Zn4	Sn5	2.547(1)×2		Na1	3.588(6)
Sn4	Zn1	2.687(1)		Na10	3.109(9)×2		Na2	3.666(6)
	Na10	2.971(6)		Na5	3.303(4)×2	Na6	Zn1	3.305(4)
	Na10	2.980(6)		Na6	3.636(4)×2		Sn5	3.321(4)
	Na1	3.221(4)		Na3	3.638(4)×2		Sn3	3.335(4)
	Na2	3.226(4)	Na1	Sn4	3.221(4)×2		Sn1	3.365(4)
	Na8	3.342(5)		M	3.234(4)		Sn4	3.396(4)
	Na9	3.346(5)		Zn1	3.263(4)		Zn3	3.421(4)
	Na7	3.370(5)		Zn2	3.276(4)		Na10	3.441(7)
	Na6	3.396(4)		Zn2	3.283(4)		Na7	3.479(6)
	Na3	3.406(4)		M	3.306(4)×2		Na5	3.530(6)
Sn5	Zn4	2.547(1)		Sn1	3.375(4)		Na3	3.538(6)
	Na7	3.259(4)		Sn1	3.531(4)		Na2	3.617(6)
	Na5	3.274(4)		Na4	3.551(6)		Zn4	3.636(4)
	Na9	3.298(5)	Na2	Zn1	3.222(4)	Na7	Sn5	3.259(4)
	Na8	3.307(5)		Sn4	3.226(4)		Zn1	3.270(5)
	Na6	3.321(4)		M	3.237(4)		Sn4	3.370(5)
	Na3	3.327(4)		Sn2	3.256(4)		Sn3	3.433(5)
	Na9	3.489(5)		Zn3	3.276(4)		Sn2	3.442(5)
	Na8	3.520(5)		Sn1	3.294(4)		Na3	3.475(6)
M	M	2.756(2)×2		Zn3	3.294(4)		Na6	3.479(6)
	Zn1	2.774(1)		Zn2	3.317(4)		Na8	3.552(7)
	Zn3	2.804(1)		Sn1	3.516(4)		Na9	3.584(6)

Atom pair		*d* / Å	Atom pair		*d* / Å	Atom pair		*d* / Å
M	Sn1	2.886(1)	Na2	Na4	3.535(6)	Na7	Na10	3.626(7)
	Sn2	2.890(1)		Na4	3.568(6)		Na10	3.654(8)
	Zn1	2.952(1)	Na9	Sn5	3.298(5)		Na8	3.704(7)
	Na1	3.234(4)		Sn4	3.346(5)	Na10	Sn4	2.971(6)
	Na2	3.237(4)		Sn2	3.427(5)		Sn4	2.980(6)
	Na1	3.306(4)		Na5	3.459(7)		Na10	3.10(2)
	Na4	3.341(4)		Sn5	3.489(5)		Zn4	3.109(9)
	Na3	3.514(4)		Na10	3.497(7)		Na6	3.441(7)
Na8	Sn5	3.307(5)		Na8	3.547(6)		Na3	3.457(7)
	Sn4	3.342(5)		Na7	3.584(6)		Na8	3.470(7)
	Sn3	3.398(5)		Na7	3.704(7)		Na9	3.497(7)
	Na5	3.429(6)		Na3	3.803(7)		Na7	3.626(7)
	Na10	3.470(7)		Na2	3.875(6)		Na7	3.654(8)
	Sn5	3.520(5)		Na9	3.930(9)			
	Na9	3.547(6)						
	Na7	3.552(7)						
	Na7	3.704(7)						
	Na6	3.783(6)						
	Na1	3.857(6)						
	Na8	3.93(1)						

Table S4. –ICOHP values for selected interatomic contacts in Na_6ZnSn_2. Energies are given in eV/bond.

interaction		*d* / Å	–ICOHP (at E_F)	–ICOHP (max.)
Sn	Zn	2.561(1)	2.74	2.74
Na	Sn	3.156(1) - 3.723(1)	0.32	0.32
Na	Zn	3.109(2) - 3.791(1)	0.12	0.16
Na	Na	3.260(1) - 3.668(1)	0.07	0.09

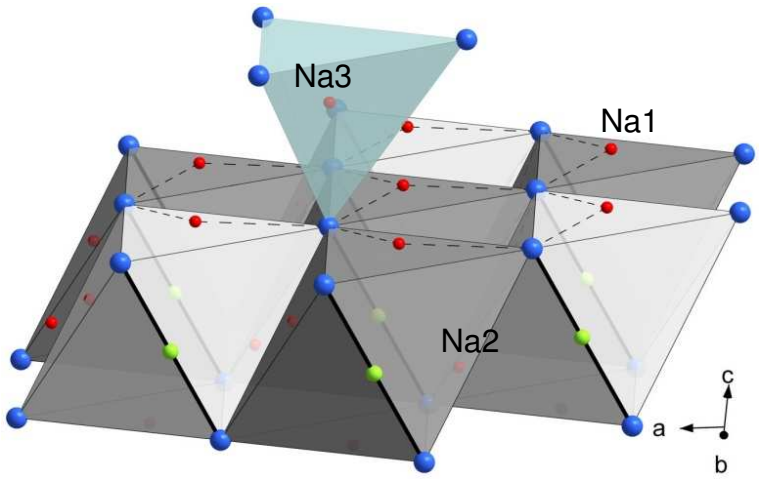


Figure S1. Projection of the structure of Na_6ZnSn_2 emphasizing the coordination environments of Na1 to Na3. The wurzite like layer formed by Na1 and Sn atoms is indicated with dashed lines. Na, Zn, Sn atoms are represented as red, green, and blue spheres, respectively.

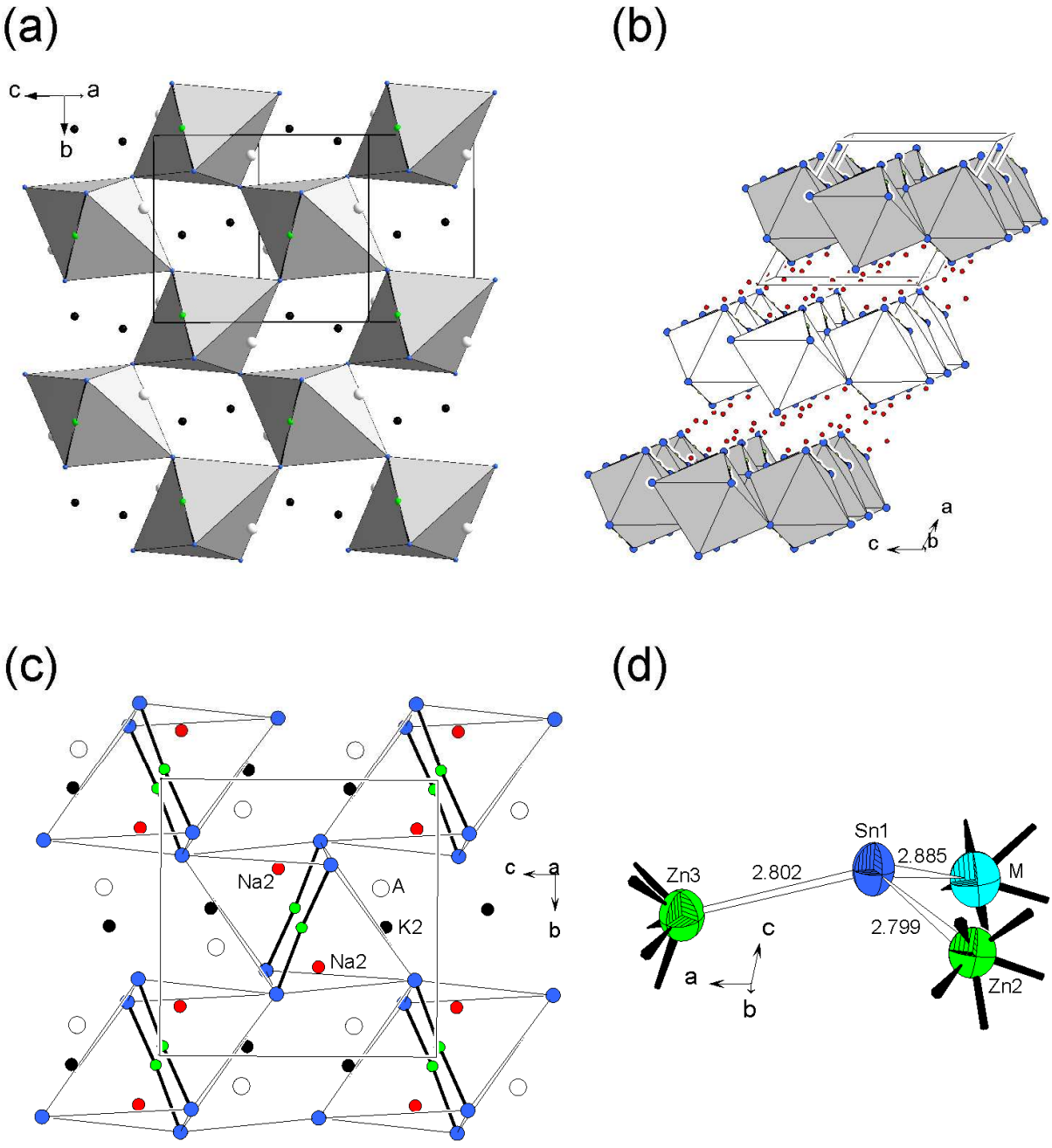


Figure S2. Further structural details for $Na_{4.24}K_{1.76(1)}ZnSn_2$ (a –c) and $Na_{20}Zn_8Sn_{11}$(d): (a) [010] view of a single layer of corner sharing distorted $\{Sn_{2/1}Sn_{4/2}\}$ octahedra. (b) Primitive stacking of these layers along *a*. (c) Distribution of the alkali atoms within a layer of $\{Sn_{2/1}Sn_{4/2}\}$ octahedra. (d) Connectivity of the Sn1 atom that interlinks three {Zn/Sn} icosahedra (atoms are drawn at 90% probability level). For angle values see structure description. Na, K, A = Na/K, Sn, Zn, and M atoms are represented as red, black, empty, blue, green, and teal spheres, respectively.

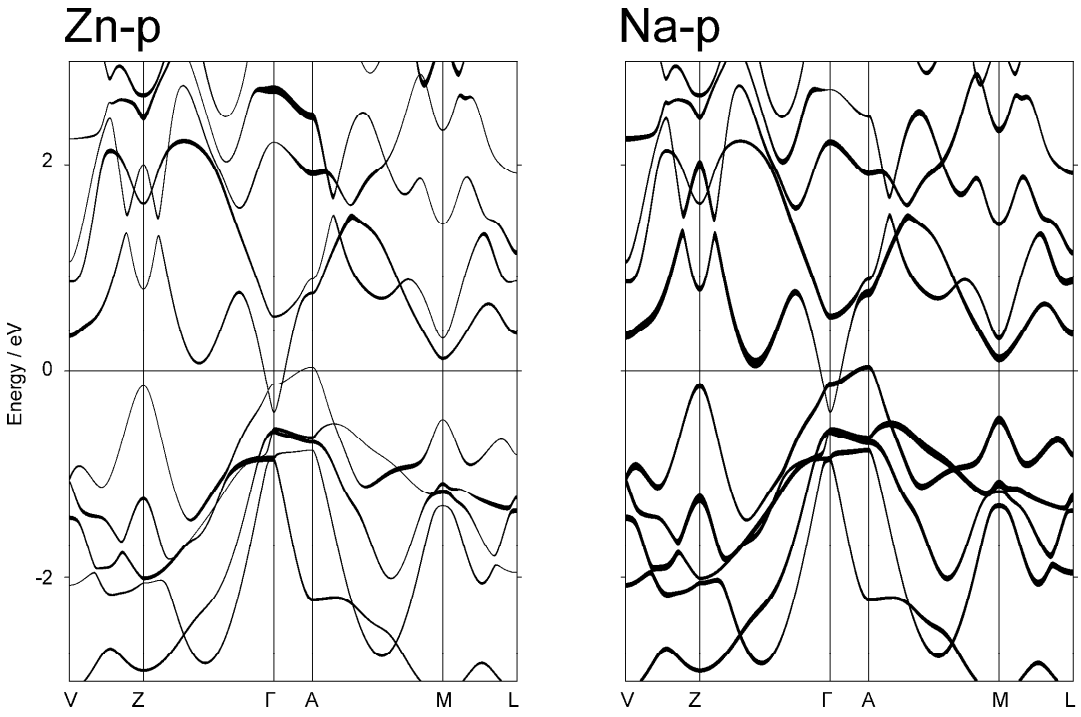
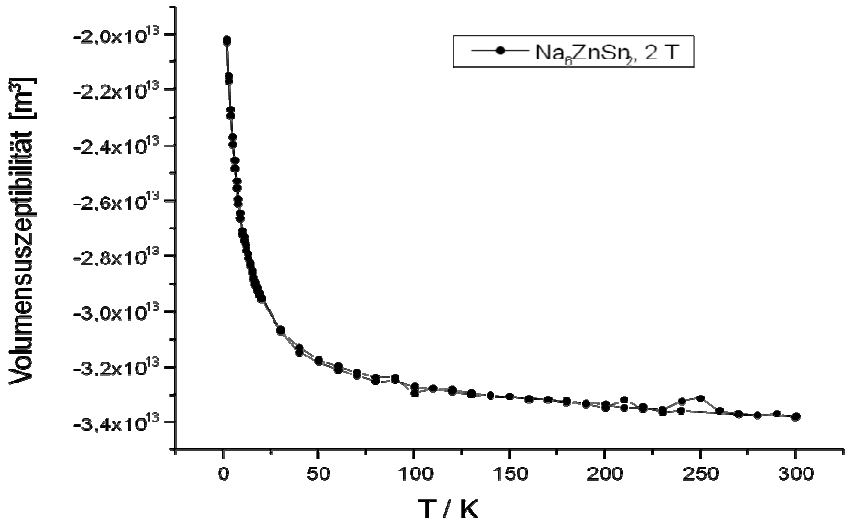
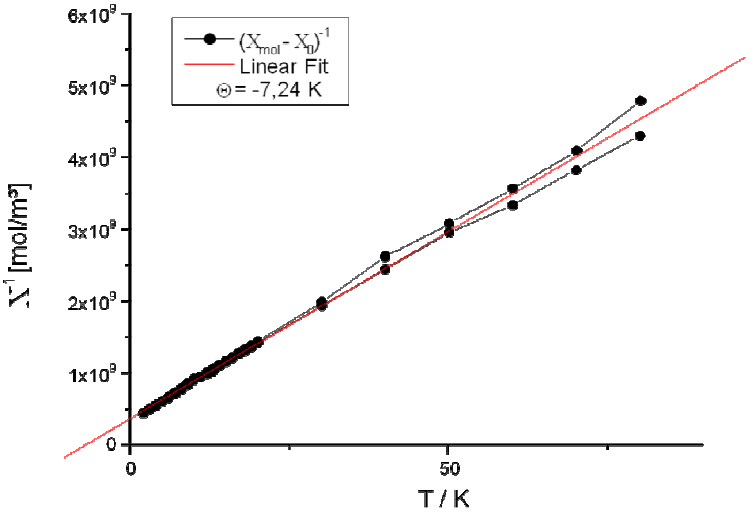


Figure S3. Fat band plots of Zn-*p* (left) and Na-*p* (right) in Na_6ZnSn_2.



(a)



(b)

Figure S4. The magnetic property of Na_6ZnSn_2. (a) From 50 to 300 K the magnetic susceptibility is almost temperature independent and negative, as expected for a diamagnetic compound. (b) Below 50 K the inverse susceptibility (χ^{-1}) is nearly linear in temperature and obeys the Curie-Weiss law with a Weiss temperature of -7.24 K. This antiferromagnetic contribution we assign to a paramagnetic impurity.

Complete reference 38.

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