Supplementary information

Crystal structure and chemical bonding of the intermetallic Zintl phase $Yb_{11}AlSb_9$

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1. Single crystal refinements of $Yb_{11}AlSb_9$ - Anisotropic displacement parameters at 15K.

Atom	site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{23} (Å^2)	U_{13} (Å^2)	U_{13} (Å^2)
Yb1	8c	0.00239(3)	0.00251(3)	0.00268(3)	0.00042(2)	0.00046(2)	0.00005(2)
Yb2	8c	0.00230(3)	0.00217(3)	0.00257(3)	0.00021(2)	-0.00048(2)	0.00000(2)
Yb3	8c	0.00285(2)	0.00241(3)	0.00200(2)	0.00006(3)	0.00004(2)	-0.00007(2)
Yb4	8c	0.00233(2)	0.00218(3)	0.00209(3)	0.00019(2)	0.00003(2)	-0.00010(2)
Yb5	8c	0.00206(2)	0.00204(3)	0.00219(3)	-0.00015(2)	-0.00001(2)	0.00002(2)
Yb6	4a	0.00218(3)	0.00204(4)	0.00308(4)	0	0	0.00022(3)
Sb1	4b	0.00201(5)	0.00207(6)	0.00209(5)	0	0	-0.00007(5)
Sb2	8c	0.00234(4)	0.00224(4)	0.00222(4)	-0.00011(4)	0.00000(3)	0.00016(3)
Sb3	8c	0.00275(4)	0.00211(4)	0.00199(4)	-0.00001(4)	-0.00005(4)	-0.00019(3)
Sb4	8c	0.00225(4)	0.00237(5)	0.00215(4)	-0.00019(4)	0.00007(3)	0.00002(3)
Sb5	8c	0.00219(4)	0.00231(5)	0.00235(4)	-0.00025(4)	-0.00014(3)	0.00018(3)
Al	4a	0.0037(4)	0.0042(4)	0.0034(4)	0	0	0.0005(3)

2. Full details on Rietveld-refinements of $Yb_{11}AlSb_9$ and $Yb_{14}AlSb_{11}$ at 90K, 300K, 500K, and 950K. Detalis on all temperature (90-1000K) are found in the cif-files.

Temperature	**90 K**	**300 K**	**500 K**	**900 K**
$N_{observations}$	3744	3744	3743	3743
$N_{reflect.}$ (11-1-9) / (14-1-11)	2849 / 3486	2926 / 3591	2955 / 3815	2968 / 3863
$N_{param.}$ (11-1-9) / (14-1-11)	39 / 5	39 / 5	39 / 5	39 / 5
$N_{parameters}$ (pattern) / (total)	62 / 76	62 / 76	62 / 76	62 / 76
Scale (11-1-9)	$1.427(8)\cdot10^{-6}$	$1.60(1)\cdot10^{-6}$	$1.43(2)\cdot10^{-6}$	$1.45(2)\cdot10^{-6}$
a [Å] (11-1-9)	11.7533 (2)	11.7945 (2)	11.8249 (4)	11.8974 (4)
b [Å] (11-1-9)	12.3782 (2)	12.4293 (2)	12.4636 (4)	12.5533 (4)
c [Å] (11-1-9)	16.6917 (3)	16.7351 (3)	16.7683 (5)	16.8474 (6)
X-parameter (11-1-9)	0.089 (7)	0.077 (8)	0.05 (2)	0.10 (2)
Y-parameter (11-1-9)	0.0300 (7)	0.0314 (8)	0.039 (2)	0.037 (2)
U_{iso}(Yb, 11-1-9) [Å^2]	-0.0003 (5)	0.0072 (6)	0.020 (2)	0.035 (2)
U_{iso}(Sb, 11-1-9) [Å^2]	-0.0018 (5)	0.004 (1)	0.016 (2)	0.029 (3)
U_{iso}(Al, 11-1-9) [Å^2]	-0.02 (1)	-0.01 (2)	-0.02 (2)	-0.02 (2)
x (Yb1, 11-1-9)	0.6865 (6)	0.6867 (7)	0.689 (1)	0.691 (1)
y (Yb1, 11-1-9)	0.5624 (5)	0.5634 (6)	0.5646 (9)	0.5660 (9)
z (Yb1, 11-1-9)	0.10 (22)	0.10 (16)	0.09 (65)	0.10 (18)
x (Yb2, 11-1-9)	0.6850 (6)	0.6847 (7)	0.681 (1)	0.682 (2)
y (Yb2, 11-1-9)	0.4469 (5)	0.4484 (6)	0.4479 (9)	0.448 (1)
z (Yb2, 11-1-9)	0.34 (22)	0.34 (16)	0.34 (65)	0.35 (18)
x (Yb3, 11-1-9)	0.6636 (4)	0.6626 (5)	0.6642 (7)	0.6642 (8)
y (Yb3, 11-1-9)	0.1729 (4)	0.1725 (4)	0.1738 (6)	0.1746 (7)
z (Yb3, 11-1-9)	0.46 (22)	0.47 (16)	0.47 (65)	0.48 (18)
x (Yb4, 11-1-9)	0.4099 (5)	0.4103 (6)	0.4127 (9)	0.4135 (9)
y (Yb4, 11-1-9)	0.2731 (6)	0.2731 (6)	0.2731 (9)	0.275 (1)
z (Yb4, 11-1-9)	0.63 (22)	0.63 (16)	0.63 (65)	0.64 (18)
x (Yb5, 11-1-9)	0.4288 (5)	0.4279 (6)	0.4286 (9)	0.428 (1)
y (Yb5, 11-1-9)	0.2743 (5)	0.2743 (6)	0.2741 (9)	0.2730 (9)
z (Yb5, 11-1-9)	0.31 (22)	0.31 (16)	0.31 (65)	0.32 (18)
z (Yb6, 11-1-9)	0.79 (22)	0.79 (16)	0.79 (65)	0.80 (18)
z (Sb1, 11-1-9)	0.22 (22)	0.22 (16)	0.22 (65)	0.23 (18)
x (Sb2, 11-1-9)	0.8677 (6)	0.8673 (6)	0.8786 (9)	0.880 (1)
y (Sb2, 11-1-9)	0.3854 (5)	0.3851 (6)	0.3827 (9)	0.3819 (9)
z (Sb2, 11-1-9)	0.46 (22)	0.47 (16)	0.46 (65)	0.47 (18)
x (Sb3, 11-1-9)	0.4641 (6)	0.4639 (7)	0.460 (1)	0.460 (2)
y (Sb3, 11-1-9)	0.3918 (5)	0.3916 (6)	0.3939 (9)	0.3932 (9)
z (Sb3, 11-1-9)	0.47 (22)	0.48 (16)	0.47 (65)	0.49 (18)
x (Sb4, 11-1-9)	0.6451 (7)	0.6449 (8)	0.644 (2)	0.645 (2)
y (Sb4, 11-1-9)	0.1342 (7)	0.1344 (7)	0.129 (2)	0.129 (2)
z (Sb4, 11-1-9)	0.65 (22)	0.66 (16)	0.66 (65)	0.67 (18)
x (Sb5, 11-1-9)	0.1809 (8)	0.1809 (9)	0.180 (2)	0.180 (2)
y (Sb5, 11-1-9)	0.3211 (7)	0.3211 (7)	0.326 (2)	0.325 (2)
z (Sb5, 11-1-9)	0.28 (22)	0.29 (16)	0.28 (65)	0.29 (18)
z (Al, 11-1-9)	0.58 (22)	0.59 (16)	0.59 (65)	0.60 (18)

Scale (14-1-11)	$2.88(9)\cdot10^{-8}$	$3.4(2)\cdot10^{-8}$	$3.6(3)\cdot10^{-8}$	$3.8(2)\cdot10^{-8}$
a [Å] (14-1-11)	16.6083 (7)	16.6616 (8)	16.739 (3)	16.8827 (3)
c [Å] (14-1-11)	22.165 (2)	22.234 (2)	22.240 (6)	22.305 (5)
X-parameter (14-1-11)	0.04 (4)	0.03 (4)	0.01 (15)	0.59 (17)
Y-parameter (14-1-11)	0.037 (4)	0.043 (4)	0.10 (2)	0.03 (2)
Zero point correction	-0.0349 (3)	-0.0380 (3)	-0.0448 (3)	-0.0388 (3)
Weight fraction 11-1-9	88.7 (8)	88.1 (8)	86 (2)	86 (2)
Weight fraction 14-1-11	11.3 (4)	11.9 (4)	13.6 (9)	14.1 (8)
R_p / R_{wp}	8.66 / 12.1	9.14 / 12.6	13.5 / 17.4	13.8 / 17.0
R_F / R_I (11-1-9)	1.58 / 3.52	1.86 / 3.53	3.49 / 5.88	3.91 / 5.74
R_F / R_I (14-1-11)	1.91 / 6.31	2.19 / 6.00	2.88 / 7.98	2.62 / 8.64
χ^2	27.1	27.4	36.5	27.6

3. Thermal expansion of the $Yb_{14}AlSb_{11}$ impurity phase

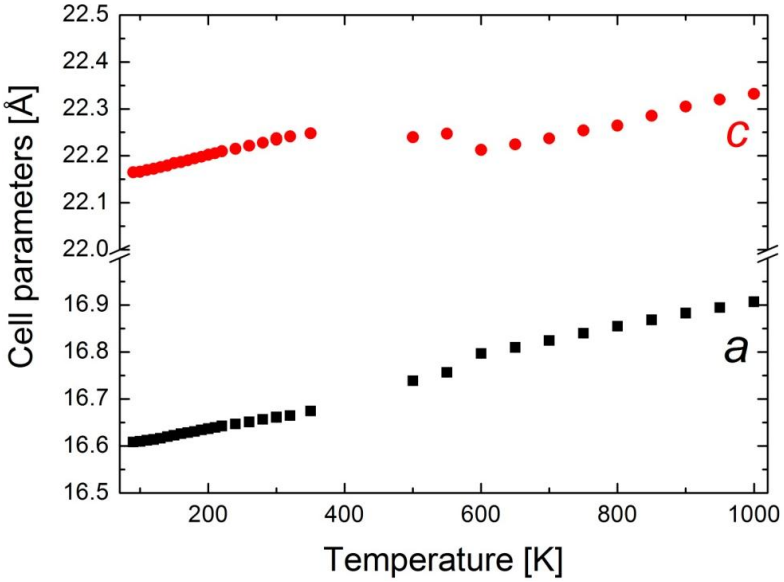


Figure 3: Lattice parameters for the tetragonal $Yb_{14}AlSb_{11}$ impurity phase from 90-350K and 500-1000K. Black squares and red circles represent cell parameters *a* and *c*, respectively. Deviations from linear expansion at higher temperatures might be due to correlations in the Rietveld refinements with the large amount of parameters.

4. Atomic displacement parameters (ADPs), Uiso(*T*), for $Yb_{11}AlSb_9$ from PXRD.

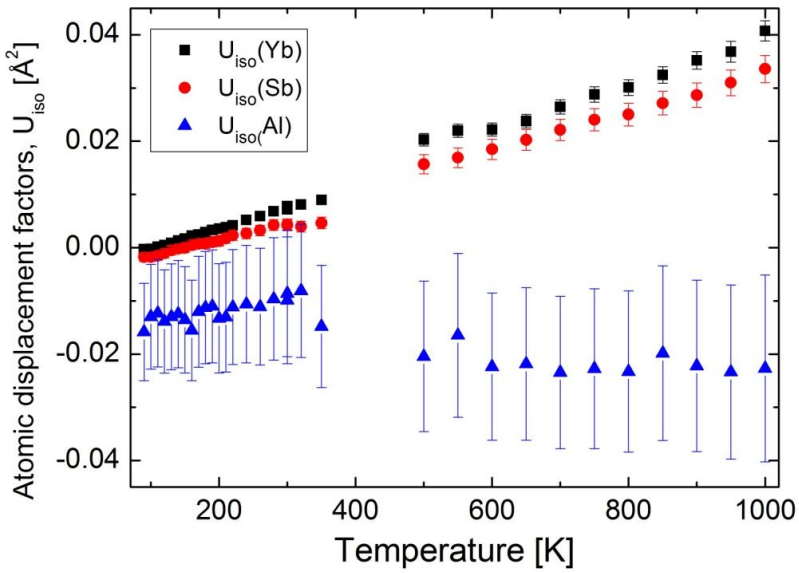
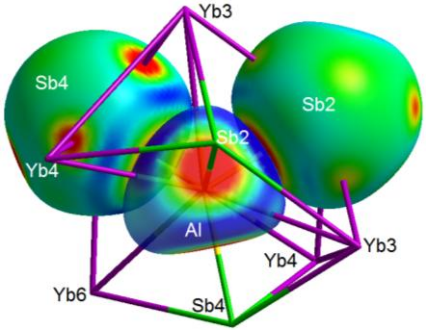


Figure 4: Constrained atomic displacement parameters of $Yb_{11}AlSb_9$ as a function of temperature. The ADPs of the light Al atom is not thrustworthy due to correlations in the refinements.

5. Atomic Hirshfeld surfaces of $Yb_{11}AlSb_9$ from PXRD at 90K

a)



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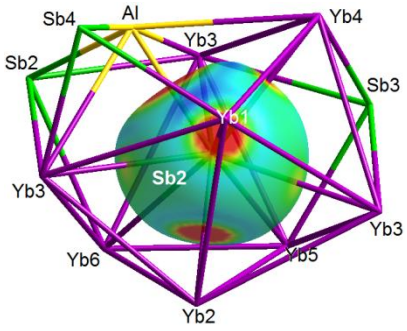

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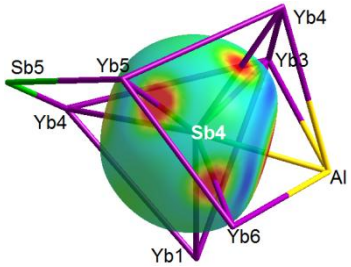

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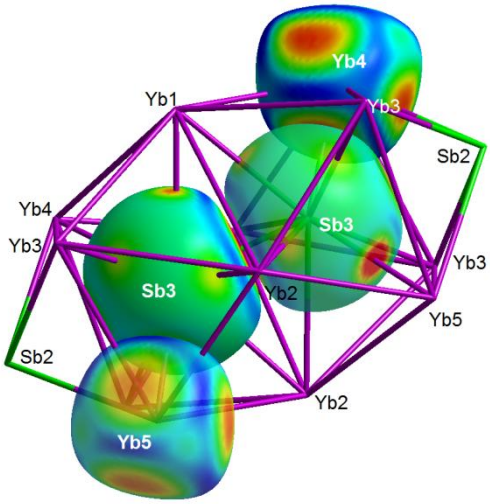
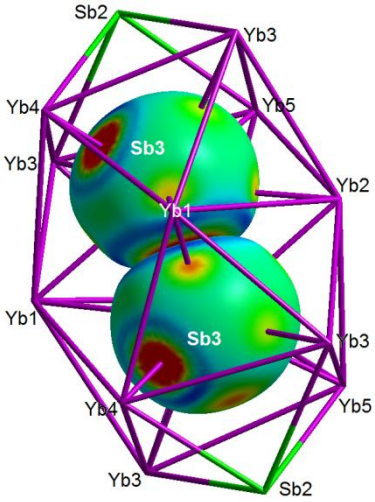


e)



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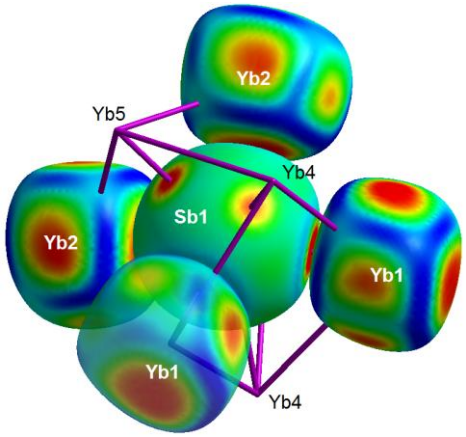
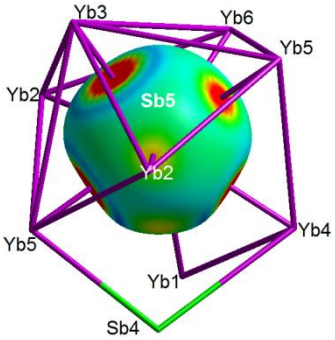


g)



h)

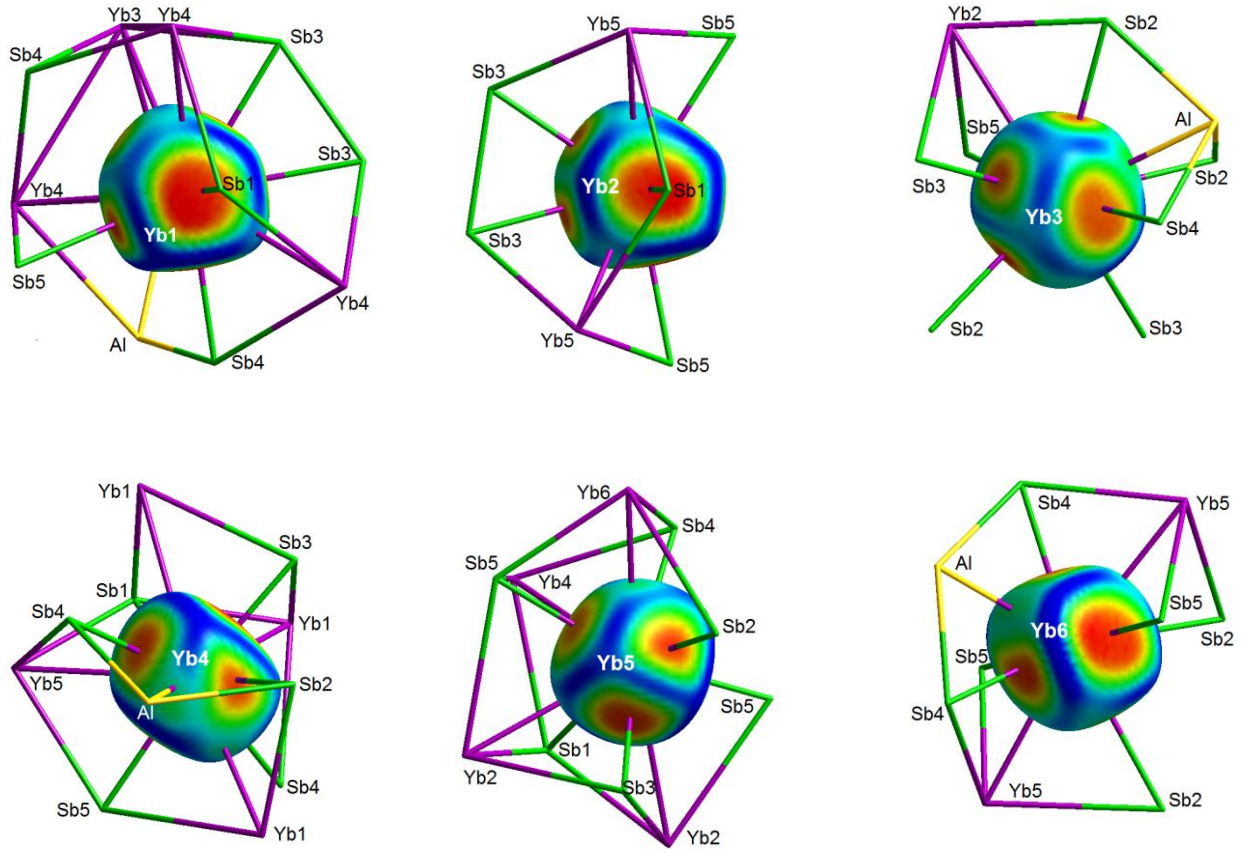


Figure 5. Curvedness plotted on the atomic Hirshfeld surfaces and mapped from -1.4 (flat; red) to -0.3 (sphere-like; blue) for the atoms of the $Yb_{11}AlSb_9$ structure at 90 K. (a)-(c) show the coordination of the atoms of the distorted tetrahedron, i.e. an aluminium atom and two of coordinated antimony atoms (Sb2 and Sb4). In (d) and (e) the symmetry-related antimony atoms of the dumbbell (Sb3) are shown. (f) and (g) show the isolated antimony atoms, while the AHS of all the ytterbium atoms are seen in (h).

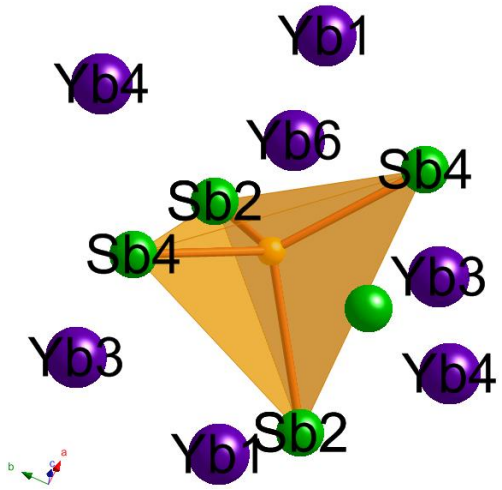
Table 5. Coordination numbers, volumes and sphericity of the Hirshfeld atoms of the $Yb_{11}AlSb_9$ structure at 90K. Coordination numbers in brackets refer to additional weaker coordinations to neighbour atoms.

Atom	Site	Structure unit	Coordination number	Volume $Å^3$	Sphericity $\pi^{1/3}(6V)^{2/3}/A$
Al	4*b*	Tetrahedron center	4	14.33	0.9572

Sb1	4*a*	Isolated anion	8	24.91	0.9922
Sb2	8*c*	Tetrahedron	6 (+ 4)	25.75	0.9939
Sb3	8*c*	Dimer	4 (+ 6)	24.47	0.9886
Sb4	8*c*	Tetrahedron	6 (+ 4)	24.86	0.9919
Sb5	8*c*	Isolated anion	5 (+ 3)	25.20	0.9920
Yb1	8*c*	Cation	7 (+ 3)	19.57	0.9817
Yb2	8*c*	Cation	7 (+ 2)	18.67	0.9807
Yb3	8*c*	Cation	7 (+ 3)	19.65	0.9836
Yb4	8*c*	Cation	6 (+ 3)	17.60	0.9801
Yb5	8*c*	Cation	6 (+ 2)	16.46	0.9811
Yb6	4*b*	Cation	6 (+ 3)	16.83	0.9807

6. Structural stability of $Yb_{11}AlSb_9$

6.1 $[AlSb_4]^{9-}$ tetrahedron

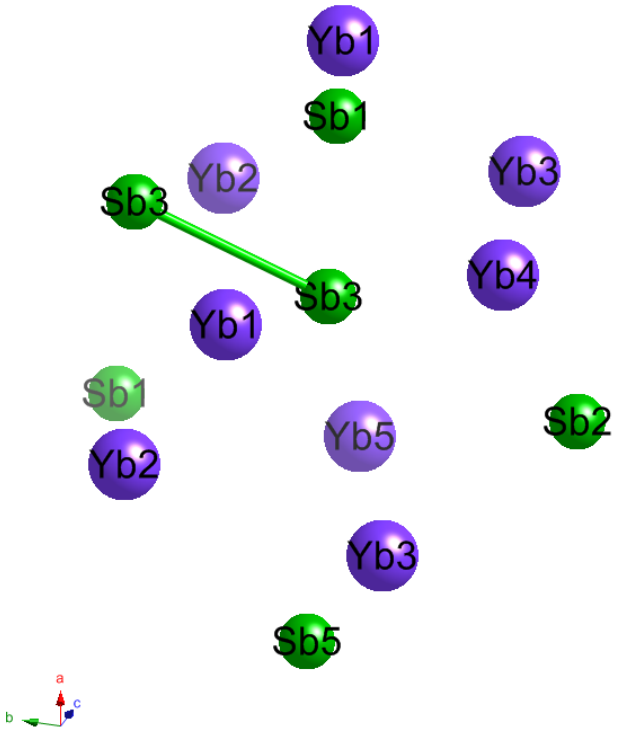


Coordination environment of the distorted tetrahedron.

Table 6.1: Distances and angles in and around the distorted tetrahedron. It is noticed that the tetrahedron distorts more from the ideal tetrahedral geometry as the temperature increases.

	15 K (single crystal)	**90K (PXRD)**	**900K (PXRD)**
Al – Sb2	2.736(2) Å	2.907442(2) Å	3.009481(2) Å
Al – Sb4	2.7644(9) Å	2.662082(1) Å	2.635607(2) Å
Al – Yb6	3.652(2) Å	3.421300(2) Å	3.350772(4) Å
Al – Yb3	3.3693(9) Å	3.483958(2) Å	3.568784(3) Å
Al – Yb4	3.6603(4) Å	3.614693(2) Å	3.665585(4) Å
Sb2-Al-Sb2	97.84(5) °	92.75576(5) °	86.3692(2) °
Sb2-Al-Sb4	107.81(1) °	105.69131(6) °	108.3200(2) °
Sb2-Al-Sb4	110.82(1) °	110.27803(7) °	109.4102(2) °
Sb4-Al-Sb4	119.57(6) °	126.87306(8) °	127.3544(2) °

6.2 $[Sb_2]^{4-}$ dimer

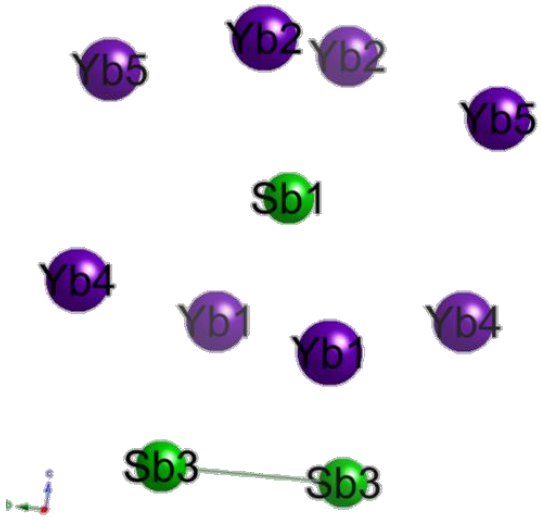


Coordination environment around the dimer.

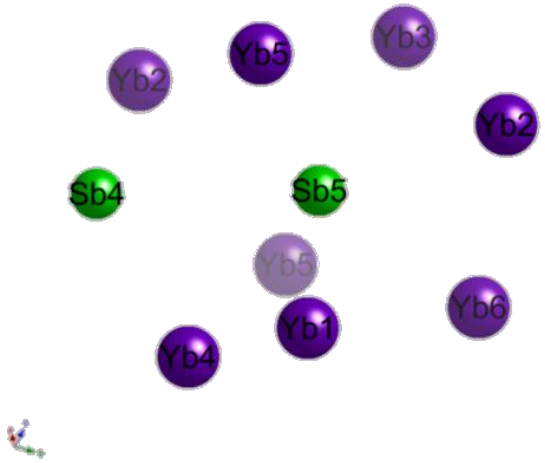
Table 6.2: Distances (in Å) around the dimer unit.

	15 K (single crystal)	**90K (PXRD)**	**900K (PXRD)**
Sb3 – Sb3	2.8267(4)	2.809063(2)	2.846269(3)
Sb3 – Yb4	3.0623(3)	3.030565(2)	3.020494(3)
Sb3 – Yb5	3.0764(3)	3.131248(2)	3.239076(3)
Sb3 – Yb1	3.3973(3)	3.392944(2)	3.417493(3)
Sb3 – Yb1	3.4719(3)	3.457100(2)	3.432341(2)
Sb3 – Yb2	3.4537(3)	3.463643(2)	3.506767(3)
Sb3 – Yb3	3.6315(3)	3.584436(2)	3.621454(4)

6.3 Isolated Sb^{3-} anions



Coordination around the Sb1 atom.



Coordination around the Sb5 atom.

Table 6.3: Distances (in Å) around the isolated Sb anions.

	15 K (single crystal)	**90K (PXRD)**	**900K (PXRD)**
Sb1 – Yb1	3.0453(3)	3.073839(2)	3.220414(3)
Sb1 – Yb2	3.0587(3)	3.042659(2)	3.007401(3)
Sb1 – Yb5 (x 2)	3.2722(2)	3.282534(4)	3.325950(3)
Sb1 – Yb4 (x 2)	3.3473(2)	3.366585(2)	3.370820(3)
Sb5 – Yb6	3.0345(2)	3.0712986(1)	3.065691(3)
Sb5 – Yb3	3.0607(3)	3.0598881(1)	3.125812(4)
Sb5 – Yb4	3.0725(3)	3.0530958(1)	3.087618(3)
Sb5 – Yb5	3.1908(3)	2.9998548(1)	3.054731(4)