Origin and effect of In-Sn ordering in $InSnCo_3S_2$: a neutron diffraction and DFT study

Jan Rothballer,[a] Frederik Bachhuber,[a,b] Stefan M. Rommel,[a] Tilo Söhnel[a,c,] and Richard Weihrich[a,*]*

Supplementary information

Content

1. VASP data including novel optimisations

Table S1: Crystal structure data from VASP PAW-PBE optimisations for partial site occupation

Scheme	In/%	Sn/%	a_{Sup}/Å	α_{Sup}/°	V_{sup}/Å³	V_{prim}/Å³	a_{rh}/Å	α_{rh}/°	a_{hex}/Å	$2a_{hex}$/Å	c_{hex}/Å
	0	100	7.598	89.976	438.500	109.660	5.374	59.980	5.372	10.744	13.164
a	12.5	87.5	7.596	89.587	438.200	109.550	5.390	59.530	5.352	10.704	13.250
b	12.5	87.5	7.600	89.927	438.920	109.730	5.377	59.920	5.371	10.741	13.179
a	37.5	62.5	7.609	88.580	440.150	110.038	5.447	58.390	5.314	10.627	13.502
b	37.5	62.5	7.611	89.829	440.870	110.218	5.390	59.800	5.373	10.747	13.222
a	50	50	7.616	88.074	441.070	110.239	5.475	57.820	5.294	10.587	13.628
b	50	50	7.617	88.457	441.370	110.361	5.458	58.250	5.313	10.626	13.543
c	50	50	7.615	89.276	441.440	110.333	5.418	59.170	5.354	10.708	13.354
d	50	50	7.616	89.754	441.700	110.425	5.397	59.720	5.374	10.748	13.247
a	62	38	7.619	89.347	442.156	110.539	5.519	58.062	5.357	10.713	13.346
b	62	38	7.618	88.201	441.453	110.363	5.471	57.965	5.301	10.603	13.603
a	88	12	7.632	88.261	443.897	110.974	5.478	58.031	5.314	10.628	13.614
b	88	12	7.628	88.562	443.411	110.853	5.461	58.366	5.326	10.651	13.539
	100	0	7.639	88.231	445.091	111.273	5.484	57.998	5.317	10.635	13.633

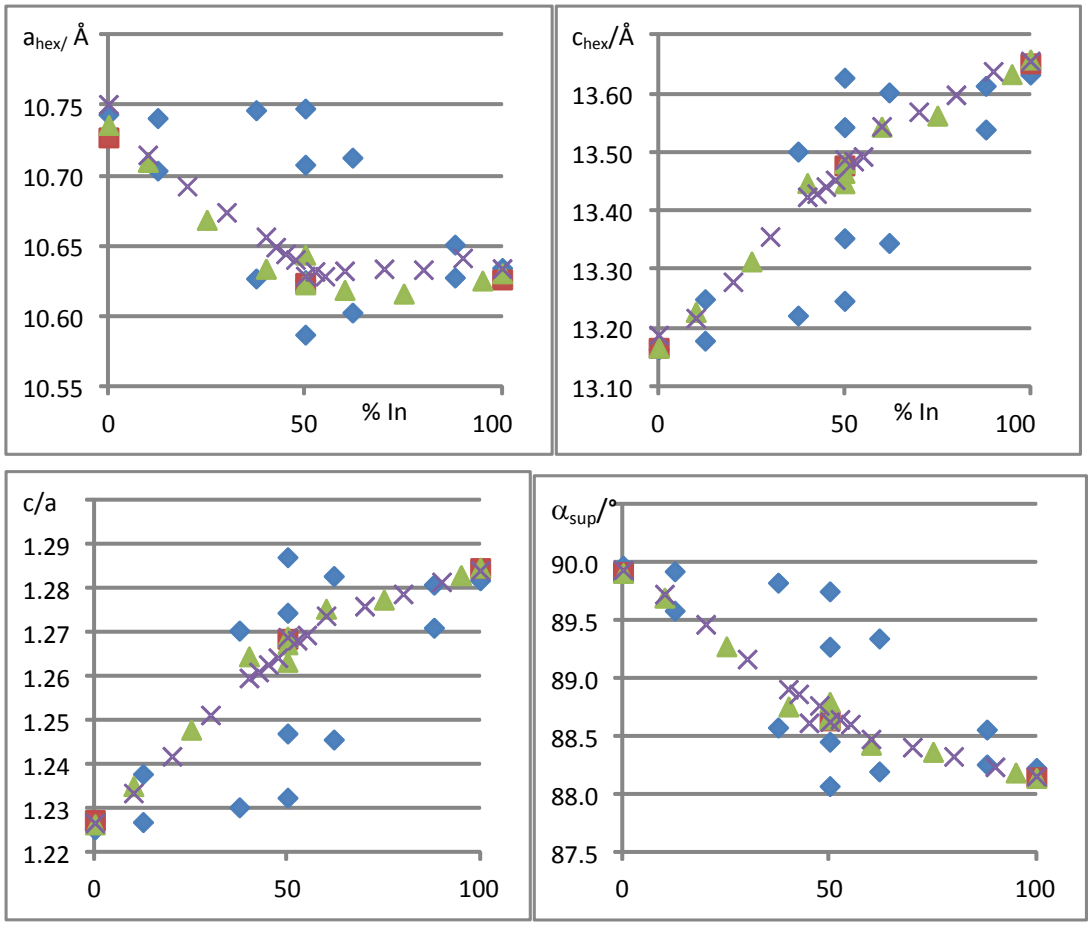

Fig. S2: Summarized crystal structure data obtained from VASP PAW-PBE optimisations for ordered structures of $In_xSn_{2-x}Co_3S_2$ (diamond symbol) and compared to experimental XRD (cross, triangle) and Neutron (square) diffraction data.

2. Comparison of VASP-PAW and CRYSTAL-PBE optimisations

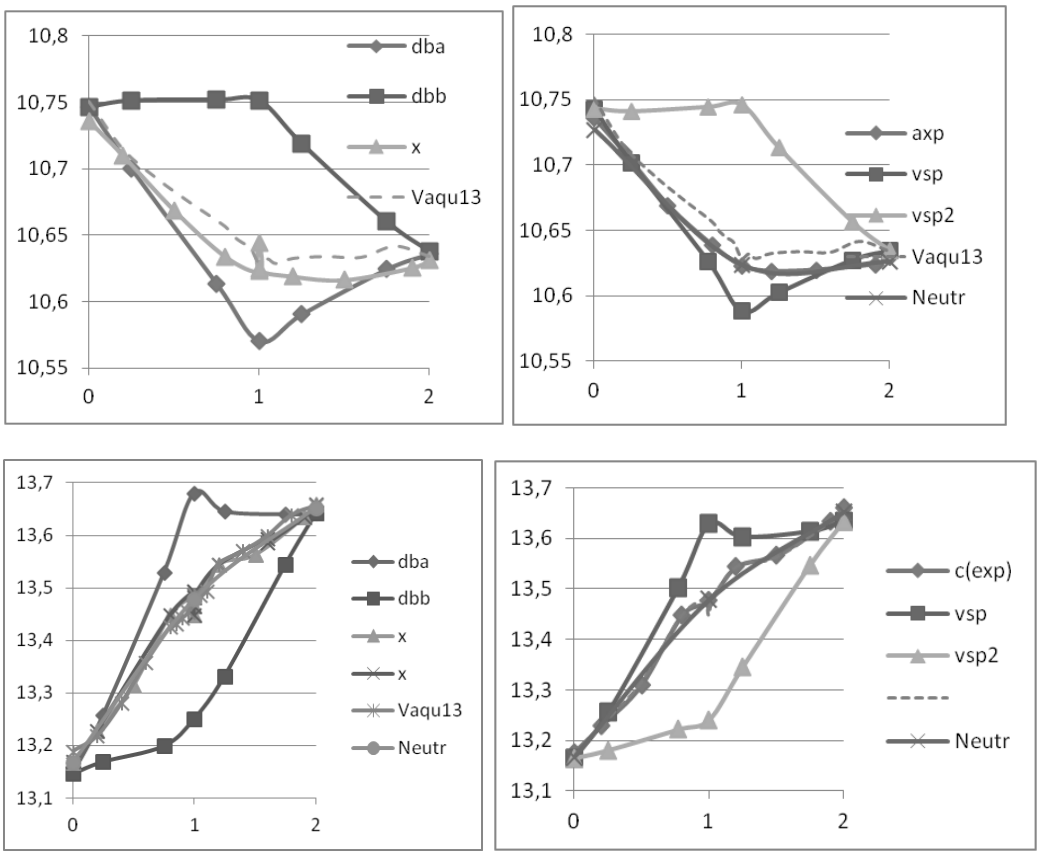

Fig. S1: Optimisations of a_{hex} (top) and c_{hex} axis (bottom) from VASP-PAW-PBE (right) and CRYSTAL-PBE (left) compared to data from Weihrich et al. (2006, Ref. 4b), Vaqueiro et al. (2013, Ref. 8), and present neutron data; dba and dbb (CRYSTAL09 calculations) as well as vsp and vsp2 denote the respective ordering variants with In and Sn preferably on A1 and A2 sites.

Table S2: Crystal structure data from VASP PAW-PBE optimisations for partial site occupation

x(In)	a_{sup}/Å	α_{sup}/°	V_{sup}/Å³	V_{rh}/Å³	2 a	a_{hex}/Å
0	7.598	89.98	438.5	109.625	10.7433	13.1647
0.25	7.596	89.57	438.2	109.55	10.702	13.25503
0.77	7.60909	88.58	440.15	110.0375	10.6267	13.502
1	7.61627	88.0745	441	110.25	10.5885	13.6278
1.25	7.61795	88.2	441.45	110.3625	10.6027	13.6027
1.75	7.6317	88.26	443.41	110.8525	10.6277	13.6139
2	7.6387	88.23	445.1	111.275	10.6346	13.6332

x(In)	a_{sup}/Å	α_{sup}/°	V_{sup}/Å³	V_{rh}/Å³	2 a	a_{hex}/Å
0	7.598	89.98	438.5	109.625	10.7433	13.1647
0.25	7.6	89.927	438.9	109.725	10.7412	13.1804
0.77	7.6095	89.82	440.9	110.225	10.7445	13.2214
1	7.614	89.77	441.7	110.425	10.7462	13.2407
1.25	7.6188	89.35	442.16	110.54	10.7133	13.3450
1.75	7.6279	88.56	443.9	110.975	10.6564	13.5466
2	7.639	88.23	445.1	111.275	10.6346	13.6332

Table S3: Crystal structure data from CRYSTAL (PBE) optimisations (from Ref. 6)

x(In)	a_{sup}/Å	α_{sup}/°	2 a_{hex}/Å	c_{hex}/Å	V_{sup}/Å³	V_{rh}/Å³
0	7.596	90.048	10.747	13.146	438.270	109.568
0.25	7.596	89.556	10.700	13.258	438.169	109.542
0.75	7.608	88.457	10.614	13.528	439.909	109.977
1	7.618	87.855	10.570	13.680	441.265	110.316
1.25	7.621	88.030	10.591	13.646	441.830	110.458
1.75	7.635	88.172	10.625	13.640	444.482	111.120
2	7.641	88.200	10.636	13.641	445.500	111.375

x(In)	a_{sup}/Å	α_{sup}/°	2 a_{hex}/Å	c_{hex}/Å	V_{sup}/Å³	V_{rh}/Å³
0	7.596	90.048	10.747	13.146	438.270	109.568
0.25	7.603	89.998	10.752	13.169	439.430	109.858
0.75	7.609	89.913	10.752	13.199	440.465	110.116
1	7.618	89.761	10.751	13.250	442.140	110.535
1.25	7.619	89.409	10.719	13.331	442.163	110.541
1.75	7.633	88.582	10.660	13.544	444.300	111.075
2	7.642	88.220	10.638	13.641	445.600	111.400

Table S4: Crystal structure data from vasp optimisations

a = 7.6164 Å, α = 88.04°
In 0,0,0
Sn 0,0,-1/2
In 0,-1/2,-1/2
Sn -1/2,-1/2,-1/2
Co -0.0000003754,-0.25,-0.25
Co 0.25,-1/2,-0.25
S 0.27860,0.77860,0.77860
S 0.27860,0.27860,0.27860

7.6165, 88.42
Sn 0,0,0
Sn 0,0,1/2
In 0,1/2,1/2
In 1/2,1/2,1/2
Co 0.0057,0.75748,0.75748
Co 0.2479,0.500,0.752093
S 0.2861,0.7769,0.776915
S 0.27383,0.2738,0.27382

7.6051, 89.37
In 0,0,0
In 0,0,-1/2
Sn 0,-1/2,-1/2
Sn -1/2,-1/2,-1/2
Co -0.00529,-0.25737,-0.25737
Co 0.25176,-1/2,-0.25176
S 0.2786,0.7786,0.7786
S 0.2786,0.2786,0.2786

7.6145, 89.77
Sn 0,0,0
In 0,0,-1/2
Sn 0,-1/2,-1/2
In -1/2,-1/2,-1/2
Co 0.0000,-0.25000,-0.2500
Co 0.2500,-1/2,-0.2500
S 0.27864,0.77864,0.77864
S 0.27864,0.27864,0.27864

3. Parameters from CRYSTAL09 calculations

Table S5: Parameters for combined cell/atom optimisation control with CRYSTAL09

Initial trust radius 0.50000 Maximum trust radius 4.00000
Max. Gradient component 0.00045 Max. displacement Component 0.00180
R.M.S. of gradient component 0.00030 R.M.S. of displacement components 0.00120
Threshold on energy change 0.100E-06 Extrapolating polynomial order 2
Maximum allowed number of steps 100 Sorting of energy points NO
Analytical gradient; hessian updating scheme: BFGS
Step size numerical gradient 0.00100
Initial hessian matrix: Schlegel model 2

Table S6: CRYSTAL basis sets

50 10
0 0 9 2.0 1.0458
3806666.0 0.0000486
563891.0 0.000387

122419.0 0.00226
31093.6 0.0112
8965.23 0.0463
2854.46 0.1549
1010.09 0.3509
400.714 0.4274
167.996 0.1915
0 1 7 8.0 1.0525
10902.6 -0.000294 0.00105
2533.25 -0.00619 0.00956
776.793 -0.0529 0.0566
275.142 -0.1471 0.217
110.753 0.1297 0.4521
51.0837 0.6009 0.4376
24.547 0.4365 0.1928
0 1 6 8.0 1.0627
237.278 0.00651 -0.0141
92.5742 -0.0316 -0.0688
38.7016 -0.3216 0.0254
17.4351 -0.00044 0.8574
8.1474 0.9163 1.2949
3.8907 0.4327 0.4281
0 3 6 10.0 1.0
353.314 0.0133
105.158 0.0929
39.3208 0.2993
16.2335 0.4698
7.0573 0.3195
2.8399 0.0524
0 1 3 8.0 1.0
7.1527 -4.6228 -0.0721
3.4236 1.5501 0.5727
1.5342 10.7304 0.9749
0 1 1 4.0 1.0
0.6743 1.0 1.0
0 3 3 10.0 1.0
5.4496 0.2114
2.1373 0.5395
0.8455 0.4545
0 3 1 0.0 1.0
0.3154 1.0
0 1 1 0.0 1.0
0.2873 1.0 1.0
0 1 1 0.0 1.0
0.14 1.0 1.0
49 10
0 0 9 2.0 1.0229
3806666.0 0.0000487
565677.0 0.000386
122672.0 0.00225
31208.0 0.0112
8973.58 0.0464
2855.32 0.1551
1009.92 0.3512
400.013 0.427
167.569 0.1887
0 1 7 8.0 1.0262
11017.4 -0.00033 0.00104
2546.93 -0.00642 0.00957
778.611 -0.0539 0.0566
275.526 -0.1475 0.2171
110.525 0.1374 0.4533
50.5711 0.6125 0.4345
24.3037 0.4209 0.1836
0 1 6 8.0 1.0314

```
      239.102   0.00648 -0.0146
       92.7375 -0.0325  -0.0705
       39.0152 -0.3244   0.0317
       17.4499  0.0117   0.8767
        8.1698  0.9158   1.2929
        3.9132  0.4324   0.441
0 3 6 10.0 1.0
      342.52    0.0128
      102.01    0.0894
       38.0838  0.2915
       15.6905  0.4663
       6.77     0.3293
       2.7107   0.0554
0 1 3 8.0 1.0
       6.5969  -4.5838  -0.0762
       3.1744   1.9149   0.5664
       1.4127   9.9244   0.8942
0 1 1 3.0 1.0
       0.6351   1.0      1.0
0 3 3 10.0 1.0
       5.0783   0.1939
       1.9711   0.5072
       0.7589   0.4477
0 3 1 0.0 1.0
       0.315    1.0
0 1 1 0.0 1.0
       0.285    1.0      1.0
0 1 1 0.0 1.0
       0.14     1.0      1.0
27 8
0 0 8 2.0  1.0
    341701.0      0.000227
     48850.0      0.001929
     10400.9      0.0111
      2718.99     0.0501
       819.661    0.1705
       283.878    0.3692
       111.017    0.4033
        46.4757   0.1433
0  1  6  8.0  1.0
      855.558   -0.0054    0.0088
      206.504   -0.0684    0.062
       69.0516  -0.1316    0.2165
       27.2653   0.2616    0.4095
       11.5384   0.6287    0.3932
        4.2017   0.2706    0.225
0  1  4  8.0     1.0
       51.5542   0.0182   -0.0287
       18.9092  -0.2432   -0.0937
        7.7251  -0.849     0.2036
        3.5428   0.8264    1.4188
0  1  1  2.0  1.0
       1.4914    1.0       1.0
0  1  1  0.0  1.0
       0.6031    1.0       1.0
0 1 1 0 1
  0.15 1 1
0 3  4  7.0  1.0
       29.9009   0.0617
       8.1164    0.2835
       2.6433    0.529
       0.8869    0.4976
0  3  1  0.0 1.0
     0.29  1.0
16 6
```

0 0 8 2.0 1.0
  109211.0 0.0002520
  16235.206 0.0019934
  3573.0286 0.0111177
  943.23811 0.0498945
  287.26179 0.1661455
  99.914226 0.3627018
  38.602137 0.4108787
  15.531224 0.1457875
0 1 6 8.0 1.0
  281.22171 -0.0057780 0.0081427
  67.106575 -0.0665855 0.0565570
  21.794135 -0.1203552 0.2039582
  8.2097646 0.2741310 0.3973328
  3.4178289 0.6463829 0.3946313
  1.5452225 0.2925792 0.1544345
0 1 3 6.0 1.0
  4.3752432 -0.1750000 -0.0613439
  1.8096201 -0.5938952 0.1272251
  0.6833985 0.8298996 1.2215893
0 1 1 0.0 1.0
  0.28 1.0 1.0
0 1 1 0.0 1.0
  0.18 1.0 1.0
0 3 1 0.0 1.0
  0.45 1.0

216 3
DURAND
0 1 3 6.0 1.0
  2.827768 -0.354607 -0.056186
  2.093537 0.688656 0.0456255
  0.491587 -0.656475 0.537546
0 1 1 0.0 1.0
  0.185 1.0 1.0
0 3 1 0.0 1.0
  0.45 1.0