



FOUNDATIONS
ADVANCES

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Supporting information for article:

Synchrotron powder diffraction of silicon: high-quality structure factors and electron density

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S1. Extraction of structure factors in *Jana2006*

The extraction of the structure factors are based on the observed and calculated powder pattern profile in the i 'th point:

$$y'_i(\text{calc}) = \sum_{h,k,l} L_i(h, k, l) A_i R_i P_i(h, k, l) \Omega_i(h, k, l) F_{hkl}^2(\text{calc}),$$

where L_i is the Lorentz, polarization and multiplicity factor, A_i is an absorption factor, R_i is a roughness correction, P_i is a preferred orientation function, and Ω_i is the reflection profile function.

The individual contributions from the reflections are determined as:

$$L_i A_i R_i P_i(h, k, l) \Omega_i(h, k, l) F_{hkl,i}^2(\text{obs}) = \frac{y'_i(\text{obs})}{y'_i(\text{calc})} L_i(h, k, l) A_i R_i P_i(h, k, l) \Omega_i(h, k, l) F_{hkl}^2(\text{calc}),$$

which reduces to:

$$F_{hkl,i}^2(\text{obs}) = \frac{y'_i(\text{obs})}{y'_i(\text{calc})} F_{hkl}^2(\text{calc}).$$

Ideally, one could calculate F^2 and $\sigma(F^2)$ as an average and the corresponding standard uncertainty.

The experimental pattern points, however, have varying uncertainties and *Jana2006* therefore applies two conditions to suppress fluctuations in the extraction of the structure-factor amplitude:

In the summation of $F^2(\text{obs})$ only the points contributing significantly are used, $\Omega_i(hkl) / \max \Omega_i(hkl) > 0.1$.

The average is weighted according to:

$$F_{hkl}^2(\text{obs}) = \frac{\sum_i w_i \frac{y'_i(\text{obs})}{y'_i(\text{calc})} F_{hkl}^2(\text{calc})}{\sum_i w_i}.$$

Since $F(\text{calc})$ is a model construction, it has no uncertainties and may thus be ignored. The weights are calculated from the standard uncertainties of:

$$Y_i = \frac{y'_i(\text{obs})}{y'_i(\text{calc})} = \frac{y_i(\text{obs}) - b_i}{y_i(\text{calc}) - b_i},$$

where b_i is the background contribution in the i 'th point. By propagation of error the standard deviation becomes:

$$\begin{aligned} \sigma^2(Y_i) = \frac{1}{w_i} = & \left(\frac{-1}{y_i(\text{calc}) - b_i} \right)^2 \sigma^2(y_i(\text{obs})) + \left(\frac{y_i(\text{obs}) - b_i}{(y_i(\text{calc}) - b_i)^2} \right)^2 \sigma^2(y_i(\text{calc})) \\ & + \left(\frac{y_i(\text{obs}) - y_i(\text{calc})}{(y_i(\text{calc}) - b_i)^2} \right)^2 \sigma^2(b_i). \end{aligned}$$

The uncertainties of b_i and $y_i(\text{calc})$ are estimated from the experimental $\sigma(y_i(\text{calc}))$:

$$\sigma(y_i(\text{calc})) = \sqrt{\frac{y_i(\text{calc})}{y_i(\text{obs})}} \sigma(y_i(\text{obs})), \text{ and } \sigma(b_i) = \sqrt{\frac{b_i}{y_i(\text{obs})}} \sigma(y_i(\text{obs}))$$

The weights thereby reduces to:

$$\frac{1}{w_i} = \sigma^2(y_i(\text{obs})) \left[\frac{1}{(y_i(\text{calc}) - b_i)^2} + \frac{y_i(\text{calc})}{y_i(\text{obs})} \left(\frac{y_i(\text{obs}) - b_i}{(y_i(\text{calc}) - b_i)^2} \right)^2 + \frac{b_i}{y_i(\text{obs})} \left(\frac{y_i(\text{obs}) - y_i(\text{calc})}{(y_i(\text{calc}) - b_i)^2} \right) \right]$$

By propagation of error and assuming zero correlation, the uncertainty of the intensity is determined to:

$$\sigma(F_{hkl}^2(\text{obs})) = \sqrt{\frac{\sum_i w_i F_{hkl}^4(\text{calc})}{\sum_i w_i}}$$

Another important practicality in the *Jana2006* software is the instability factor. This parameter should be set to 0 in a powder-pattern fitting, since it is a single-crystal function that artificially increases the uncertainty of the intense reflections.

S2. Anharmonic contribution

The anharmonic contribution was modelled by including the symmetry allowed third order term of the Gram-Charlier expanded the ADP. Table S1 lists the Rietveld refinement result of the last Wilson iteration (U_{iso} determined from a Wilson plot) and the anharmonic model. At 100 K the inclusion of the anharmonic ADPs gives an increase in the R-factor and no improvement in pattern fit (R_p). At 298 K the inclusion of anharmonic ADPs results in a small reduction of the weighted Bragg residual (wR) but no improvement of the pattern fit.

The residual density maps and the refined probability density functions are shown in Figure S1 and Figure S2.

Table S1 Rietveld refinement results of the Wilson iteration and when applying an anharmonic model.

	w2 (100 K)	Anh. (100K)	w2 (298 K)	Anh. (298 K)
R/wR	1.72/0.70	1.93/0.73	1.29/0.59	1.30/0.58
R_p/wR_p	1.08/1.13	1.08/1.13	1.12/0.90	1.12/0.90
GOF	3.69	3.69	2.62	2.52

Scale	0.9022(4)	0.9007(5)	0.9662(4)	0.9646(7)
Shift [10^{-2}°]	-	.	0.074(3)	0.074(3)
asym	-0.020(1)	-0.021(1)	-0.032(1)	-0.032(1)
a [\AA]	5.430657(9)	5.430657(9)	5.431230	5.431230
GW	2.238(7)	2.233(7)	2.333(6)	2.329(7)
LX	0.804(6)	0.799(6)	0.696(5)	0.693(5)
LY	3.84(7)	3.94(7)	2.37(6)	2.43(6)
$U_{\text{iso}} \cdot 10^{-4} [\text{\AA}^2]$	31.81	31.1(2)	56.20	55.6(2)
C123 $\cdot 10^{-4}$	-	-0.7(8)	-	-1.9(8)
κ	0.98(1)	0.98(1)	0.98(1)	0.98(1)
κ'	1.33(4)	1.30(4)	1.21(4)	1.18(4)
P32-	0.35(3)	0.36(2)	0.36(3)	0.38(3)
P40	-0.15(3)	-0.16(4)	-0.21(5)	-0.25(6)

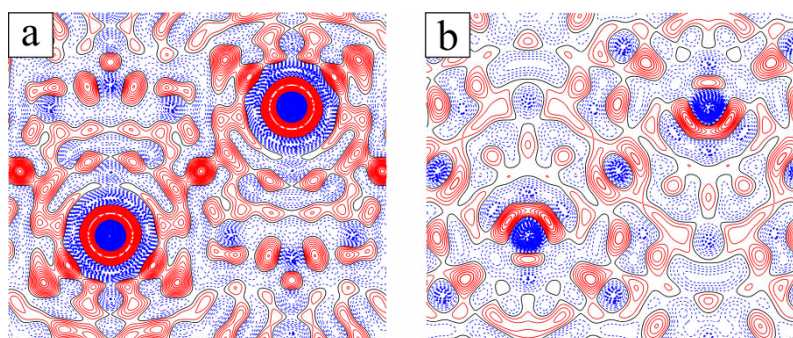


Figure S1 Residual density of (a) 100 K and (b) 298 K anharmonic models. Solid (red) lines: positive density, dotted (blue) lines: negative density, and dashed (black) lines: zero density. Contour level: $0.05e/\text{\AA}^3$

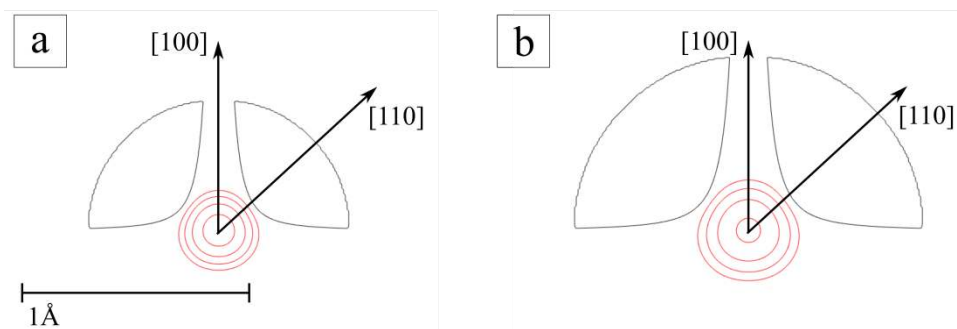


Figure S2 The atomic probability density function in the (110)-plane. The indicated [110]-direction is toward the nearest neighbor. Black line: zero density contour. Red lines: 10^{-1} , 1, 10^1 , 10^2 , ect.

S3. Residual density maps

The extracted structure-factors were subjected to an extended multipolar modelling. The corresponding residual maps are shown in Fig. S1 and S2. Note that the resolution is quite different in the two data sets, and direct comparison should be done with care.

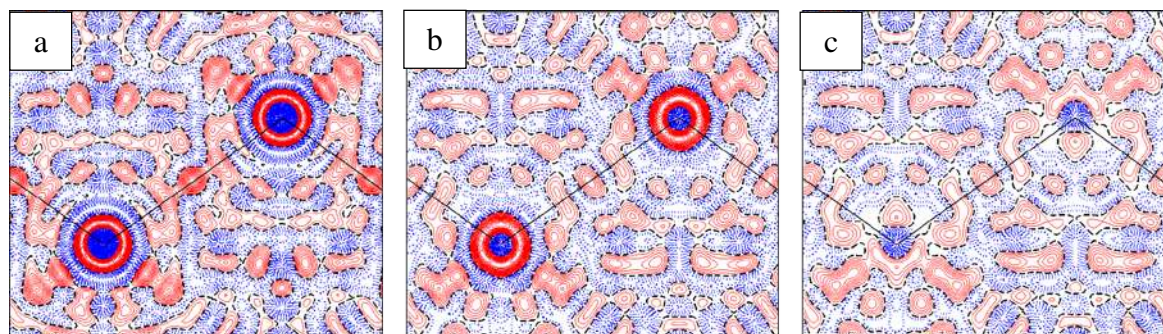


Figure S3 Residual Fourier map of 100K (a) w2-, (b) HC- and (c) EHC-models. Solid (red) lines: positive density, dotted (blue) lines: negative density, and dashed (black) lines: zero density. Contour level: $0.05e/\text{\AA}^3$

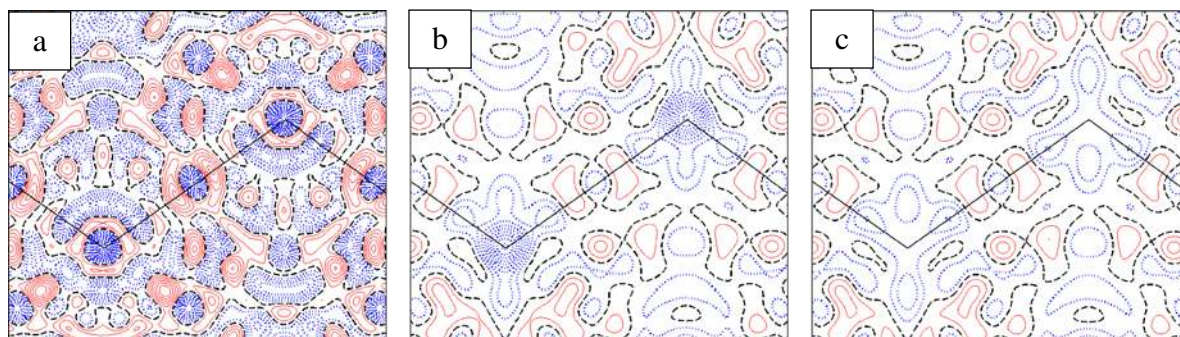


Figure S4 Residual Fourier map of 298K (a) w2-, (b) HC- and (c) EHC-models. Solid (red) lines: positive density, dotted (blue) lines: negative density, and dashed (black) lines: zero density. Contour level: $0.05e/\text{\AA}^3$

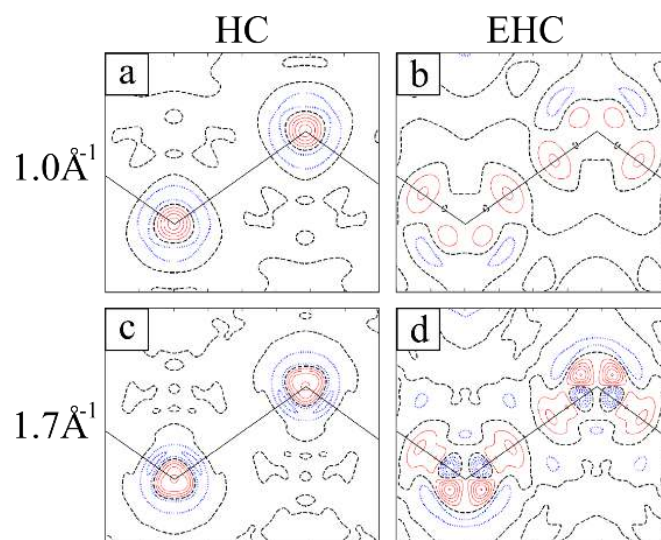


Figure S5 Residual Fourier map of theoretical data: (a) + (c) HC- and (b) + (d) EHC-models. Cut-off: (a) + (b) 1.0\AA^{-1} and (c) + (d) 1.7\AA^{-1} . Solid (red) lines: positive density, dotted (blue) lines: negative density, and dashed (black) lines: zero density. Contour level: HC: $0.05e/\text{\AA}^3$ and EHC: $0.01e/\text{\AA}^3$

S4. Extracted structure factors

Table S2 W2 -100 K

h	k	l	<i>F</i>	$\sigma(F)$
1	1	1	59.705	0.04224
2	0	2	67.861	0.03843
1	1	3	44.134	0.02308
2	2	2	1.9409	0.04827
0	0	4	57.133	0.0404
3	1	3	39.378	0.02175
2	2	4	51.051	0.02624
3	3	3	33.911	0.01907
1	1	5	34.126	0.01919
4	0	4	45.123	0.03248
3	1	5	30.41	0.01686
2	0	6	39.849	0.025
3	3	5	27.247	0.02408

4	4	4	35.808	0.04741
5	1	5	24.339	0.0185
1	1	7	24.339	0.0185
4	2	6	32.433	0.02015
5	3	5	22.041	0.01644
3	1	7	22.042	0.01644
0	0	8	28.859	0.07944
3	3	7	19.943	0.03303
6	0	6	26.592	0.02424
2	2	8	26.596	0.02425
5	5	5	18.302	0.02113
5	1	7	18.313	0.02114
4	0	8	24.406	0.03484
1	1	9	16.596	0.01946
5	3	7	16.589	0.01945
6	4	6	22.219	0.03815
3	1	9	15.233	0.02797
4	4	8	20.596	0.04265
3	3	9	14.075	0.02269
7	1	7	14.075	0.02269
5	5	7	14.08	0.0227
6	2	8	19.101	0.02111
2	0	10	19.103	0.02111
7	3	7	13.162	0.02492
5	1	9	13.159	0.02491
5	3	9	12.327	0.0378
4	2	10	16.572	0.03217
1	1	11	11.397	0.04184
7	5	7	11.394	0.04183

8	0	8	15.294	0.1189
5	5	9	10.771	0.0211
7	1	9	10.773	0.0211
3	1	11	10.773	0.0211
6	0	10	14.643	0.03763
6	6	8	14.643	0.03763
7	3	9	9.9283	0.03543
3	3	11	9.9299	0.03544
8	4	8	13.654	0.06272
0	0	12	13.654	0.06272
7	7	7	9.3355	0.04795
5	1	11	9.3346	0.04794
6	4	10	13.103	0.03172
2	2	12	13.103	0.03172
5	3	11	9.0348	0.03204
7	5	9	9.0361	0.03205
4	0	12	11.879	0.09039
9	1	9	8.3396	0.12504
8	2	10	11.734	0.05249
7	1	11	7.9437	0.03077
9	3	9	7.9442	0.03078
5	5	11	7.9442	0.03078
1	1	13	7.9438	0.03077
4	4	12	10.411	0.10498
7	3	11	7.7686	0.03311
3	1	13	7.7684	0.03311
7	7	9	7.7677	0.0331
6	2	12	10.401	0.05819
9	5	9	7.153	0.08438

3	3	13	7.1533	0.08438
8	8	8	9.5892	0.37169
5	1	13	7.2143	0.04857
7	5	11	7.214	0.04857
8	6	10	9.757	0.04258
2	0	14	9.7571	0.04258
10	0	10	9.757	0.04258
5	3	13	6.7735	0.05173
9	1	11	6.7735	0.05173
8	0	12	8.9006	0.14598
9	7	9	6.1167	0.07126
9	3	11	6.1163	0.07125
10	4	10	8.9311	0.0422
6	6	12	8.9311	0.0422
4	2	14	8.9311	0.0422
5	5	13	6.0217	0.0596
7	1	13	6.0218	0.0596
7	7	11	6.022	0.0596
8	4	12	8.8508	0.08425
7	3	13	5.9374	0.05107
9	5	11	5.9376	0.05107
1	1	15	5.9374	0.05107
6	0	14	7.9505	0.17984
3	1	15	6.0008	0.12866
3	3	15	5.2976	0.06445
7	5	13	5.2977	0.06445
11	1	11	5.2976	0.06445
9	9	9	5.2975	0.06445
10	2	12	7.8276	0.05506

6	4	14	7.8276	0.05506
9	1	13	5.4429	0.04214
9	7	11	5.4429	0.04214
11	3	11	5.443	0.04214
5	1	15	5.443	0.04214
0	0	16	5.5684	1.0026
9	3	13	5.4048	0.08069
5	3	15	5.4047	0.08069
2	2	16	7.1878	0.05888
8	2	14	7.1878	0.05888
10	8	10	7.1878	0.05888
11	5	11	4.1195	0.17463
7	7	13	4.1195	0.17463
4	0	16	6.938	0.1241
8	8	12	6.938	0.1241
7	1	15	4.8831	0.0698
9	5	13	4.8831	0.0698
5	5	15	4.8832	0.06981
10	6	12	6.7168	0.13379
7	3	15	4.4583	0.12824
9	9	11	4.4584	0.12824
12	0	12	6.7018	0.18378
4	4	16	6.7018	0.18378
1	1	17	4.7449	0.09552
11	7	11	4.7449	0.09552
11	1	13	4.7449	0.09552
8	6	14	6.509	0.05855
6	2	16	6.509	0.05855
10	0	14	6.509	0.05855

11	3	13	4.4678	0.05363
9	7	13	4.4678	0.05363
3	1	17	4.4678	0.05363
7	5	15	4.4678	0.05363
12	4	12	6.632	0.31992
3	3	17	4.4003	0.14946
9	1	15	4.4003	0.14946
10	4	14	5.3347	0.16355
5	1	17	4.1893	0.07643
9	3	15	4.1893	0.07643
11	5	13	4.1893	0.07643
8	0	16	5.1117	0.36296
11	9	11	4.0893	0.11957
5	3	17	4.0893	0.11957
7	7	15	4.0893	0.11957
6	6	16	5.2432	0.18761
2	0	18	5.2432	0.18761
9	5	15	3.8598	0.17821
9	9	13	3.8598	0.17821
8	4	16	5.0988	0.19169
7	1	17	3.5776	0.09324
11	7	13	3.5776	0.09324
5	5	17	3.5776	0.09324
13	1	13	3.5776	0.09324
12	2	14	5.256	0.07867
10	10	12	5.256	0.07867
4	2	18	5.256	0.07867
11	1	15	3.1635	0.12178
7	3	17	3.1635	0.12178

13	3	13	3.1636	0.12179
12	8	12	5.4131	0.4273
9	7	15	3.8936	0.14921
11	3	15	3.8936	0.14921
10	8	14	4.5815	0.08839
10	2	16	4.5815	0.08839
6	0	18	4.5815	0.08839
7	5	17	3.3628	0.14671
11	11	11	3.3628	0.14671
1	1	19	3.3627	0.14671
13	5	13	3.3627	0.14671

Table S3 W2 – RT

h	k	l	<i>F</i>	$\sigma(F)$
1	1	1	59.927	0.04763
2	0	2	67.009	0.05464
1	1	3	43.543	0.0338
2	2	2	1.7517	0.05145
0	0	4	55.763	0.04834
3	1	3	38.204	0.03135
2	2	4	49.093	0.03912
1	1	5	32.86	0.02806
3	3	3	32.748	0.02796
4	0	4	42.821	0.04172
3	1	5	28.896	0.02736
2	0	6	37.532	0.03461
3	3	5	25.298	0.02904
4	4	4	33.223	0.0524
5	1	5	22.436	0.02351

1	1	7	22.445	0.02351
4	2	6	29.51	0.02751
3	1	7	20.011	0.02017
5	3	5	20.015	0.02018
0	0	8	26.487	0.08006
3	3	7	17.875	0.03541
6	0	6	23.626	0.02902
2	2	8	23.629	0.02902
5	1	7	16.185	0.02324
5	5	5	16.177	0.02323
4	0	8	21.072	0.03687
5	3	7	14.403	0.02179
1	1	9	14.407	0.0218
6	4	6	19.3	0.0412
3	1	9	13.107	0.02928
4	4	8	17.53	0.04429
5	5	7	11.968	0.02424
7	1	7	11.965	0.02424
3	3	9	11.965	0.02424
2	0	10	16.091	0.02362
6	2	8	16.091	0.02361
7	3	7	10.832	0.02598
5	1	9	10.83	0.02598
5	3	9	10.157	0.04063
4	2	10	13.634	0.03443
1	1	11	9.2508	0.04429
7	5	7	9.2495	0.04428
8	0	8	12.485	0.12293
5	5	9	8.664	0.02273

3	1	11	8.6646	0.02274
7	1	9	8.6649	0.02274
6	6	8	11.711	0.04123
6	0	10	11.711	0.04123
3	3	11	7.9855	0.03884
7	3	9	7.9849	0.03884
0	0	12	10.899	0.06556
8	4	8	10.899	0.06556
7	7	7	7.5864	0.05199
5	1	11	7.586	0.05199
2	2	12	10.31	0.03419
6	4	10	10.31	0.03419
5	3	11	7.0973	0.03528
7	5	9	7.0978	0.03528
4	0	12	8.899	0.09903
9	1	9	6.1694	0.143
8	2	10	8.8582	0.05674
7	1	11	6.1734	0.03378
9	3	9	6.1736	0.03378
1	1	13	6.1734	0.03378
5	5	11	6.1736	0.03378
4	4	12	8.6244	0.12171
3	1	13	5.8366	0.03777
7	3	11	5.8367	0.03777
7	7	9	5.8364	0.03776
6	2	12	7.9506	0.06849
3	3	13	5.5713	0.09776
9	5	9	5.5712	0.09776
8	8	8	8.0793	0.47632

7	5	11	5.1149	0.05409
5	1	13	5.115	0.05409
8	6	10	7.2176	0.04758
10	0	10	7.2176	0.04758
2	0	14	7.2176	0.04758
9	1	11	4.9358	0.0596
5	3	13	4.9358	0.0596
8	0	12	6.0344	0.18059
9	7	9	4.4103	0.08623
9	3	11	4.4102	0.08622
10	4	10	6.4316	0.04961
4	2	14	6.4316	0.04961
6	6	12	6.4316	0.04961
7	1	13	4.4859	0.07183
5	5	13	4.4859	0.07183
7	7	11	4.4859	0.07183
8	4	12	5.7708	0.10266
7	3	13	3.7522	0.06227
9	5	11	3.7523	0.06227
1	1	15	3.7522	0.06227
6	0	14	5.1299	0.23287
3	1	15	3.705	0.16863
3	3	15	3.625	0.08134
7	5	13	3.6251	0.08134
9	9	9	3.625	0.08134
11	1	11	3.625	0.08134
6	4	14	5.211	0.06617
10	2	12	5.211	0.06617
9	1	13	3.6168	0.05559

11	3	11	3.6168	0.05559
5	1	15	3.6168	0.05559
9	7	11	3.6168	0.05559
0	0	16	5.8527	1.2818
9	3	13	3.3366	0.10399
5	3	15	3.3365	0.10399
2	2	16	4.5638	0.07666
10	8	10	4.5638	0.07666
8	2	14	4.5638	0.07666
7	7	13	2.8465	0.23436
11	5	11	2.8465	0.23436
8	8	12	5.0426	0.16235
4	0	16	5.0426	0.16235
5	5	15	3.3564	0.09352
7	1	15	3.3564	0.09352
9	5	13	3.3564	0.09352
10	6	12	4.418	0.17207
9	9	11	2.5783	0.18217
7	3	15	2.5783	0.18217
4	4	16	3.5801	0.25687
12	0	12	3.5801	0.25687
11	1	13	2.8468	0.13689
11	7	11	2.8469	0.13689
1	1	17	2.8468	0.13689
8	6	14	4.2512	0.07884
6	2	16	4.2512	0.07884
10	0	14	4.2512	0.07884
11	3	13	2.923	0.0716
9	7	13	2.923	0.0716

7	5	15	2.923	0.0716
3	1	17	2.923	0.0716
