Supporting information

S1. Theoretical Electron density models

The theoretical structure factors are of a quality and resolution which probes the inner atom density. In such a case the pseudo-atoms is divided into shells with flexible multipole parameter (Fischer *et al.* 2011):

$$\rho_{\mathrm{at}}(\mathbf{r}) = \sum_{n=1}^{N}\left[P_n\kappa_n^3\rho_n(\kappa_n r) + \sum_{l=0}^{l_{\max}}\kappa_n'^{\,3}R_{l,n}(\kappa_n' r)\sum_{m=0}^{l}P_{nlm\pm}d_{lm\pm}(\theta,\varphi)\right] \qquad \text{(S1)}$$

where P_n denotes the electronic population of the shell n. The aspherical redistribution is modeled by real spherical harmonics, $d_{lm\pm}$, with individual population parameters, $P_{nlm\pm}$ (l and m refer to the order of the spherical harmonic function in question). Radial expansion and contraction of the atomic ED are regulated by κ and κ'.

Table S1 and Figure S1 show the results when refining increasingly complex models against the theoretical data. The individually refined shells are based on the orbitals and the form-factor composition. The names in Table S1 and Figure S1 are based on which 'orbitals' are refined. Since the multipole functions are basis-functions in the description of the total ED, the population parameter values are not to be confused with number of the given type of electrons. The ordinary Hansen-Coppens model (HC), where only the valence ED is explicitly refined is in here called 4s+3d.

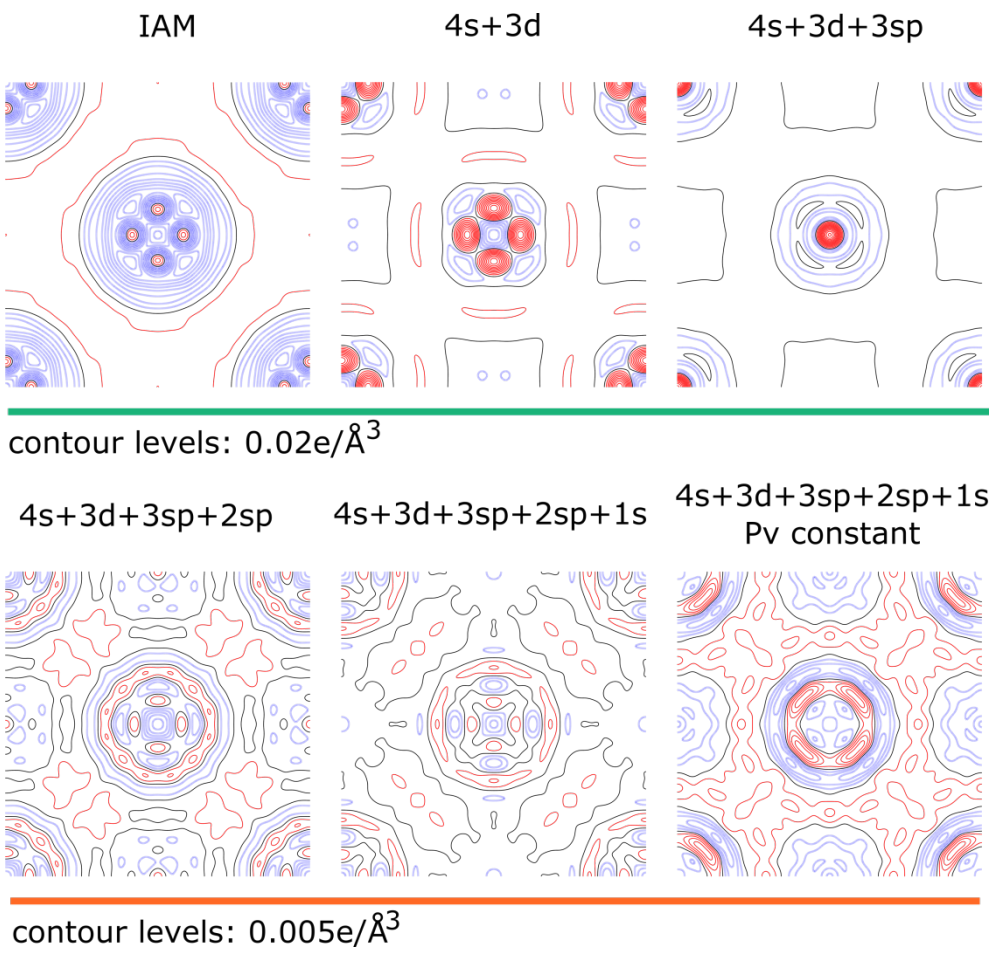

Figure S1 Difference Fourier maps of theoretical data and the different static ED models.

Table S1 Parameters of the different multipole models. If no standard deviations are given the parameter has not been refined.

	IAM	3d+4s	3sp+3d+4s	2sp+3sp+3d+4s	1s+2sp+3sp+3d+4s	1s+2sp+3sp+3d+4s -$\mathbf{P_v}$
R/wR [%]	0.16/0.43	0.07/0.09	0.04/0.06	0.02/0.02	0.01/0.01	0.03/0.04
GOF	0.03	0.01	0.00	0.00	0.00	0.00
1s: $\mathbf{P_v}/\boldsymbol{\kappa}$	2.00/1.00	2.00/1.00	2.00/1.00	2.00/1.00	2.00/1.56(9)	2.00/0.98(1)
2sp: $\mathbf{P_v}/\boldsymbol{\kappa}$	8.00/1.00	8.00/1.00	8.00/1.00	8.30(2)/0.973(2)	8.56(2)/0.937(3)	8.00/1.0020(5)
3sp: $\mathbf{P_v}/\boldsymbol{\kappa}$	8.00/ 1.00	8.00/ 1.00	8.01(2)/ 1.0050(8)	9.36(8)/ 1.0201(4)	10.28(10)/ 1.0121(9)	8.00/ 1.012(1)
P40	0.00	0.00	0.015(2)	0.0149(6)	0.0148(4)	0.015(1)

3d: $\mathbf{P_v}/\boldsymbol{\kappa}$	10.00/ 1.00	10.000(5)/ 1.0017(5)	9.99(2)/ 0.996(1)	8.3(1)/ 0.895(6)	7.2(1)/ 0.827(7)	10.00/ 0.987(1)
P40/P60	0.00/ 0.00	-0.131(9)/ 0.202(6)	-0.121(6)/ 0.186(5)	-0.073(3)/ 0.108(4)	-0.058(3)/ 0.079(4)	-0.105(5)/ 0.164(4)
4s: $\mathbf{P_v}/\boldsymbol{\kappa}$	1.00/1.00	1.00/1.00	1.00/1.00	1.00/1.00	1.00/1.00	1.00/1.00
BCP						
$\boldsymbol{\rho}$ [e/Å^3]	0.2304	0.2580	0.2578	0.2608	0.2632	0.2578
$\boldsymbol{\nabla^2\rho}$ [e/Å^5]	2.0647	1.6286	1.6703	1.8072	1.7991	1.7395

S1.1. Anharmonic ADPs

The theoretical structure factors provided means to investigate the effect of the refining anharmonic ADPs in the case of purely isotropic displacement. By folding the static structure factors with an isotropic ADP it was possible to refine the Gram-Charlier parameters in JANA2006 (Petricek *et al*. 2014). Table S2 and Figure S2 illustrates that this is possible to some degree, however due to the weak features in the core ED this is only a minor effect.

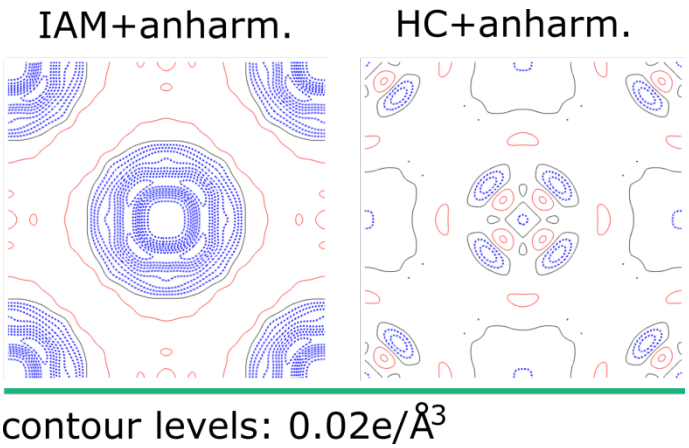

Figure S2 Difference Fourier maps when anharmonic displacement is modelled. HC = 4s+3d.

Table S2 Parameters of the harmonic and anharmonic models. If no standard deviations are given the parameter has not been refined.

	IAM	IAM + anh.	HC	HC + anh.
R/wR	0.16/0.43	0.14/0.43	0.07/0.09	0.05/0.08

GOF	0.03	0.03	0.01	0.01
3d: $\mathbf{P_v}/\boldsymbol{\kappa}$	11.00/1.00	11.00/1.00	11/1.0016(4)	11/1.0023(5)
P40/P60	0.00/0.00	0.00/0.00	-0.132(9)/0.203(5)	-0.134(8)/0.206(5)
$\boldsymbol{U_{iso}}$ [10^{-4}Å^2]	28.00	28.10(17)	28.00	28.08(4)
D^{1111}/D^{1122}	0/0	1.89(211)/-0.02(56)	0/0	0.73(55)/-0.23(13)
F^{111111}/F^{111122}	0/0	73(96)/2(13)	0/0	26(22)/-4(3)

S2. Rietveld refinements:

Table S3 and S5 lists the results of the Rietveld iterations. At RT the a few iterations was needed before the isotropic displacements determined by a Wilson plot had reached convergence. Table S4 and S6 list the post-Rietveld refinement results.

Table S3 Low temperature Rietveld-refinement results. If no standard deviations are given the parameter has not been refined.

	LT-1	**LT-2**
R/wR	0.88/0.97	0.75/0.85
Rp/wRp	2.27/1.96	2.28/1.97
GOF	5.53	5.54
Scale	1.1317(8)	1.1344(6)
sycos	0.65(1)	0.64(1)
Asym	-0.175(4)	-0.174(4)
a (Å)	3.60476(2)	3.604757(18)
GW	1.87(1)	1.88(1)
LX/LY	0.748(7)/1.8(2)	0.751(7)/1.7(2)
LYe	9.1(3)	9.0(2)
U_{iso} (10^{-4} Å^2)	27.68(12)	27.90
κ	1.0016	1.0016
P_{40}	-0.132	-0.132

P_{60}	0.203	0.203
D^{1111}	0	-2.93
D^{1122}	0	0.03
F^{111111}	0	-72
F^{111122}	0	-3

Table S4 LT post-Rietveld refinements. If no standard deviations are given the parameter has not been refined.

	IAM – LT1	**HC – LT1**	**HC+Anh – LT1**	**IAM – LT2**	**HC – LT2**	**HC+Anh – LT2**
R/wR [%]	0.76/0.87	0.77/0.87	0.76/0.84	0.82/0.90	0.81/0.91	0.76/0.84
GOF	0.41	0.41	0.41	0.43	0.43	0.41
Scale	1.0013	1.0013	1.0013	1.0037	1.0037	1.0037
U_{iso} (10^{-4} Å^2)	28.36	28.36	27.9(6)	27.90	27.90	28.5(6)
D^{1111}	0	0	-2.93(348)	0	0	-1.56(352)
D^{1122}	0	0	0.03(93)	0	0	0.75(94)
F^{111111}	0	0	-72(156)	0	0	-34(157)
F^{111122}	0	0	-3(23)	0	0	8(23)

Table S5 RT Rietveld-refinement results. If no standard deviations are given the parameter has not been refined. W1and W2 is the first and second refinement imposing U_{iso} determined from a Wilson plot.

	RT-1	**RT-1 (W1)**	**RT-1 (W2)**	**RT-2**
R/wR	1.15/1.27	0.93/0.98	0.93/0.98	0.88/0.95
Rp/wRp	1.85/1.72	1.88/1.74	1.89/1.73	1.90/1.73
GOF	5.09	5.10	5.11	5.11
Scale	1.0696(9)	1.0655(6)	1.0659(6)	1.0660(6)
sycos	0.45(2)	0.44(2)	0.44(2)	0.44(2)
Asym	-0.130(5)	-0.127(5)	-0.127(5)	-0.126(5)

a (Å)	3.61523(3)	3.61524(3)	3.61524(3)	3.615247(31)
GW	1.97(1)	1.98(1)	1.98(1)	1.99(1)
LX/LY	0.695(9)/5.1(3)	0.695(9)/4.9(3)	0.697(9)/4.9(3)	0.700(9)/4.82(27)
Lye	7.4(3)	7.4(3)	7.4(3)	7.4(3)
U_{iso} (10^{-4} Å^2)	63.79(20)	65.21	65.34	65.34
D^{1111}	0	0	0	-10.32
D^{1122}	0	0	0	-1.77
F^{111111}	0	0	0	-521
F^{111122}	0	0	0	-82
Wilson plot				
U_{iso} (10^{-4} Å^2)	65.21(29)	65.34(29)	65.35(29)	65.41(29)
Scale	1.016(5)	1.007(5)	1.003(5)	1.0031(5)

Table S6 RT post-Rietveld refinements. If no standard deviations are given the parameter has not been refined.

	IAM – RT1	**HC – RT1**	**HC+Anh – RT1**	**IAM – RT2**	**HC – RT2**	**HC+Anh – RT2**
R/wR [%]	1.13/1.02	1.03/1.01	0.98/0.95	1.14/1.02	1.03/1.01	0.97/0.93
GOF	0.51	0.50	0.49	0.51	0.50	0.49
Scale	1.003	1.003	1.003	1.0031	1.0031	1.0031
U_{iso} (10^{-4} Å^2)	65.35	65.35	65.5(9)	65.41	65.41	64.5(9)
D^{1111}	0	0	-10.32(693)	0	0	-11.87(678)
D^{1122}	0	0	-1.77(181)	0	0	-1.82(177)
F^{111111}	0	0	-521(400)	0	0	-570(392)
F^{111122}	0	0	-82(57)	0	0	-93(56)

S3. Manual background

The background and capillary intensity is shown in Figure S3 alongside the diffractogram at LT and RT. Note that the intensity from 1° to 3° is almost identical in the three data sets. The manual

background of the RT data is more 'oscillating' caused by the higher TDS contribution. The higher background in the Cu-scattering data at higher angle is a result of Compton scattering and TDS.

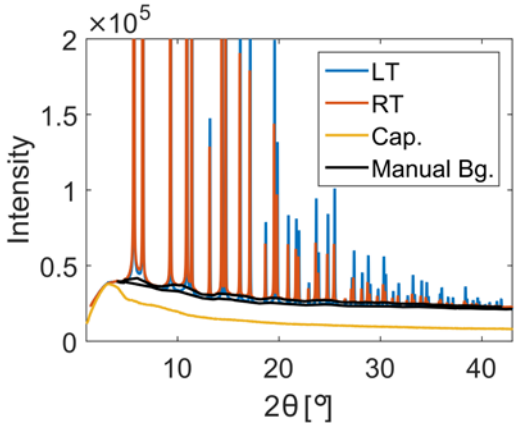

Figure S3 The LT, RT and capillary (measured at RT) scattering intensity scaled to the same intensity at $2\theta = 3^{o}$. The manual background is depicted in black.

S4. Experimental residual density maps

Figure S4 and S4 shows the unweighted residual density maps.

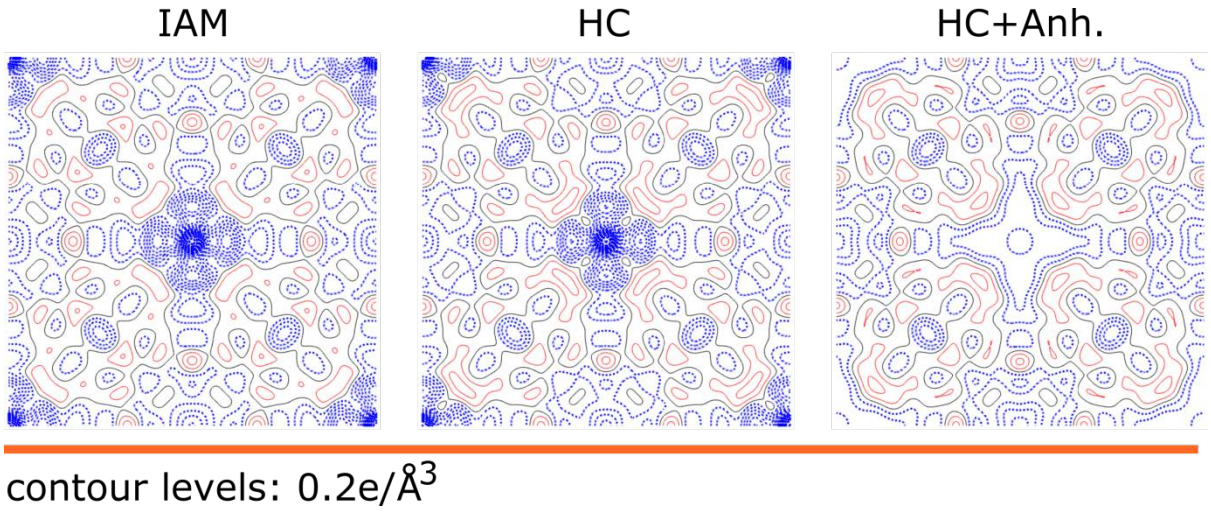

Figure S4 LT residual density maps in the (100)-plan.

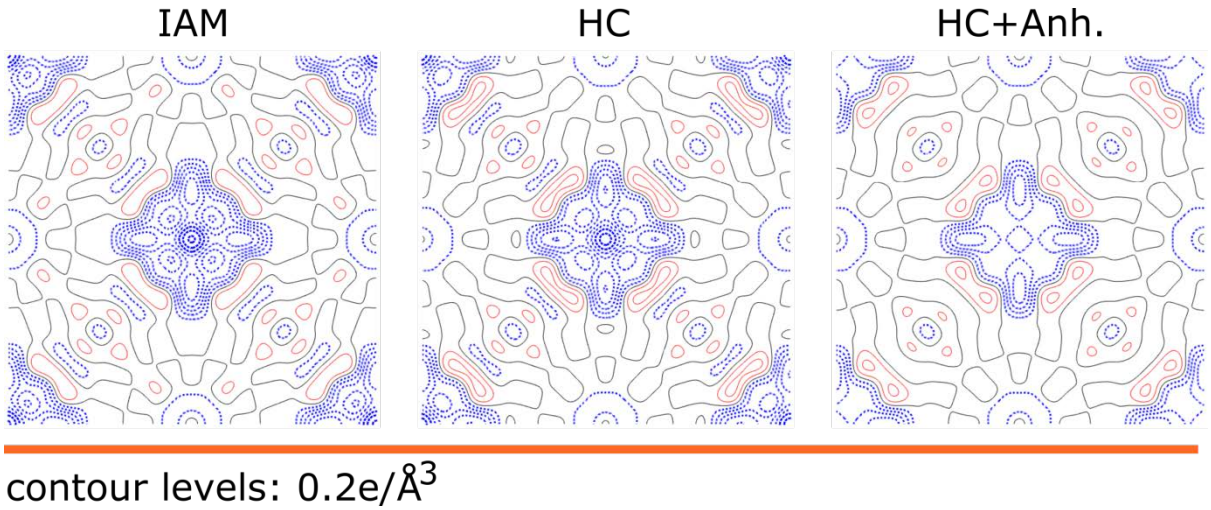

Figure S5 RT residual density maps in the (100)-plan.

S5. Probability density function error

The error in the PDF was determined by Monte-Carlo simulations in Jana2006.

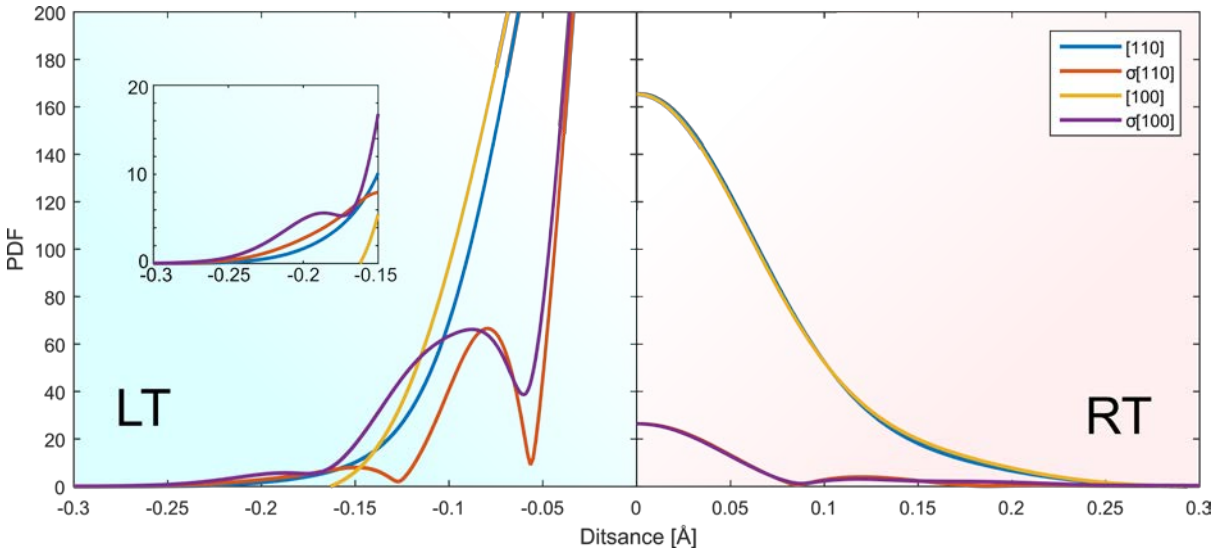

Figure S6 PDF and error

S6. Extracted structure factors

Table S7 Extracted structure factors from LT data (95(3) K)

h	*k*	*l*	*F*	*σ*(*F*)
1	1	1	86.368	3.284

0	0	2	79.795	3.399
2	0	2	63.884	1.186
1	1	3	56.056	1.304
2	2	2	54.131	0.838
0	0	4	45.709	1.004
3	1	3	42.311	0.669
2	0	4	40.89	0.622
2	2	4	37.004	0.457
1	1	5	34.158	0.507
3	3	3	34.122	0.452
4	0	4	30.549	0.654
3	1	5	29.361	0.397
4	2	4	28.827	0.400
0	0	6	28.824	0.412
2	0	6	26.519	0.755
3	3	5	26.147	0.698
2	2	6	25.37	0.640
4	4	4	24.017	0.531
1	1	7	23.123	0.540
5	1	5	23.129	0.525
4	0	6	23.051	0.341
4	2	6	22.253	0.405
3	1	7	21.393	0.333
5	3	5	21.401	0.324
0	0	8	19.686	0.644
3	3	7	19.808	0.383
4	4	6	19.743	0.283
2	0	8	19.720	0.289
2	2	8	18.530	0.353

6	0	6	18.536	0.307
5	5	5	18.250	0.192
5	1	7	18.246	0.207
6	2	6	18.213	0.260
4	0	8	17.110	0.300
5	3	7	17.069	0.221
1	1	9	17.032	0.223
4	2	8	16.875	0.230
6	4	6	16.195	0.264
3	1	9	15.629	0.242
4	4	8	15.21	0.317
7	1	7	14.887	0.404
3	3	9	14.872	0.409
5	5	7	14.899	0.405
6	0	8	14.701	0.406
0	0	10	14.661	0.406
2	0	10	14.288	0.413
6	2	8	14.323	0.391
5	1	9	13.869	0.475
7	3	7	13.884	0.470
6	6	6	13.602	0.441
2	2	10	13.559	0.450
5	3	9	13.066	0.652
4	0	10	12.939	0.519
6	4	8	12.973	0.516
4	2	10	12.397	0.489
1	1	11	12.053	0.339
7	5	7	12.124	0.329
8	0	8	11.242	0.837

3	1	11	11.454	0.387
7	1	9	11.489	0.367
5	5	9	11.498	0.367
4	4	10	11.376	0.463
8	2	8	11.374	0.438
6	6	8	11.226	0.292
6	0	10	11.198	0.313
7	3	9	10.794	0.516
3	3	11	10.762	0.526
6	2	10	10.59	0.508
0	0	12	10.169	0.527
8	4	8	10.264	0.484
5	1	11	9.7523	0.5663
7	7	7	9.7900	0.5323
2	0	12	10.108	0.790
6	4	10	9.6825	0.4343
2	2	12	9.6256	0.4340
5	3	11	9.5098	0.4840
7	5	9	9.5420	0.4763
4	0	12	9.2429	0.7616
9	1	9	9.2707	0.6067
8	6	8	8.8069	0.4300
8	0	10	8.7866	0.4349
4	2	12	8.749	0.4370
8	2	10	8.5309	0.5532

Table S8 Extracted structure factors from RT data (~ 293 K)

h	*k*	*l*	*F*	$\sigma(F)$
1	1	1	84.523	2.031

0	0	2	77.658	1.964
2	0	2	61.208	2.411
1	1	3	52.869	0.726
2	2	2	50.709	0.802
0	0	4	41.748	0.794
3	1	3	38.318	0.507
2	0	4	36.811	0.590
2	2	4	32.517	0.524
1	1	5	29.542	0.307
3	3	3	29.556	0.286
4	0	4	25.84	0.382
3	1	5	24.341	0.277
4	2	4	23.811	0.237
0	0	6	23.771	0.245
2	0	6	21.336	0.347
3	3	5	20.778	0.468
2	2	6	20.03	0.335
4	4	4	18.862	0.584
5	1	5	17.459	0.361
1	1	7	17.414	0.365
4	0	6	17.256	0.303
4	2	6	16.366	0.307
5	3	5	15.344	0.206
3	1	7	15.319	0.213
0	0	8	13.992	1.065
3	3	7	13.793	0.386
4	4	6	13.45	0.241
2	0	8	13.404	0.248
6	0	6	12.355	0.310

2	2	8	12.312	0.311
5	1	7	11.954	0.187
5	5	5	11.949	0.174
6	2	6	11.896	0.287
4	0	8	11.128	0.361
5	3	7	10.622	0.223
1	1	9	10.571	0.235
4	2	8	10.474	0.252
6	4	6	9.7187	0.4454
3	1	9	9.3108	0.2393
4	4	8	8.8220	0.6976
3	3	9	8.5648	0.2009
7	1	7	8.5988	0.1862
5	5	7	8.5726	0.1856
6	0	8	8.4076	0.4436
0	0	10	8.3487	0.4928
2	0	10	8.0599	0.2611
6	2	8	8.1110	0.2546
5	1	9	7.6447	0.2446
7	3	7	7.6457	0.2394
2	2	10	7.4595	0.4890
6	6	6	7.4618	0.4265
5	3	9	7.1351	0.3697
4	0	10	6.8167	0.4121
6	4	8	6.8195	0.4046
4	2	10	6.2409	0.5266
7	5	7	5.8387	0.4951
1	1	11	5.8265	0.5102
8	0	8	5.4857	1.4393

3	1	11	5.5821	0.2417
7	1	9	5.62	0.2254
5	5	9	5.5811	0.2239
8	2	8	5.9309	0.4859
4	4	10	5.9091	0.4855