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Compressibility and crystal structure of andalusite at high pressure

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Abstract

The unit-cell dimensions and crystal structure of andalusite Al_2SiO_5 have been refined from X-ray data on single crystals mounted in a diamond anvil cell at pressures of 12, 25, and 37 kbar. Structure refinements with anisotropic temperature factors yielded weighted R factors of 3.4, 4.9, and 5.2% respectively. The bulk modulus of andalusite is 1.35±0.10 mbar and the axial compression ratios of orthorhombic unit-cell axes $a:b:c$ are approximately 2.1:1.5:1.0. The relatively greater compressibility of the Al(1)–O_D bond results in a being the most compressible axis. Those bonds that compress $>3\sigma$ between 1 bar and 37 kbar at room temperature, are the bonds that also expand significantly between 25 and 1000°C at room pressure. Polyhedral bulk moduli for the Al(1) octahedron, the Al(2) trigonal bipyramid and the Si tetrahedron are 1.3±0.2, 1.6±0.5, and 4.1±1.5 mbar, respectively. Thus, the aluminum polyhedra are significantly more compressible than the silicon tetrahedron. The omega step-scanning technique of X-ray intensity data collection results in a significant improvement in accuracy and is recommended for structure determination with the diamond-anvil high-pressure cell.

Introduction

High pressure structure determination contain valuable data on the equations of state, interatomic forces and chemical bonding in minerals. The Al_2SiO_5 polymorphs, andalusite, sillimanite and kyanite, provide an interesting system where aluminum occurs in three types of coordinations; in addition to the octahedral coordination found in all three minerals, aluminum also occurs in tetrahedal coordination in sillimanite and in five-fold trigonal bipyramidal coordination in andalusite. Knowledge of the response to pressure and temperature of these different types of Al–O bonds in the presence of relatively rigid SiO_4 tetrahedra is necessary for an understanding of the stability relations and phase transformation within the Al_2SiO_5 system. The temperature effects on the crystal structures of andalusite, sillimanite and kyanite have been determined by Winter and Ghose (1979). The elastic constants of andalusite and sillimanite have been determined by Vaughan and Weidner (1978), who used the Brillouin scattering technique. From infrared and Raman spectroscopic data, the phonon spectra of andalusite and their temperature dependence have been determined and interpreted on the basis of a rigid-ion model by Iishi et al. (1979).

In this paper are presented data on the high pressure structural response of andalusite to 37 kbar, as well as correlations between high-pressure changes and high-temperature response, elasticity, and phonon spectra. It has been possible to observe directly the structural elements of andalusite that are responsible for the compressibility and, hence, the elastic constants. The present data on andalusite at high-pressure, combined with high-temperature data of Winter and Ghose (1979), may be used to test the inverse relationship between structural responses due to temperature versus pressure (Hazen and Finger, 1982). Andalusite is a light-atom structure with a small unit-cell and orthorhombic symmetry and thus also constitutes a test case for the improvement in accuracy of X-ray intensity data collected at high pressure by the omega step-scanning technique. The resulting improvement in

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Table 4a. Calculated and observed structure factors for andalusite at 12 kbar; continuous scan data.

H	OBS	CALC
0 K 0		
0	0	3200
2	163	165
4	488	480
6	216	202
1 K 0		
1	479	439
2	404	402
3	235	248
4	153	157
5	349	354
6	249	251
7	271	282
8	148	175
2 K 0		
0	202	202
1	369	361
2	738	761
3	112	120
4	112	96
5	419	424
6	455	473
7	55	31
8	79	79
3 K 0		
1	514	516
2	707	682
3	185	150
5	181	178
6	290	290
7	323	324
8	73	11
9	170	162
4 K 0		
0	366	371
1	320	321
3	105	95
4	688	745
5	211	222
7	64	42
8	283	274
9	166	179
5 K 0		
1	462	476
2	160	174
3	89	118
4	58	99
5	164	89
8	100	84
9	184	183
10	94	55
6 K 0		
0	444	438
1	249	260
2	518	511
4	277	276
5	204	209
6	353	346
8	180	180
9	212	212
10	272	277
7 K 0		
1	114	103
3	562	579
4	107	89
5	307	310
6	112	102
7	172	176
8	131	117
9	122	88
8 K 0		
0	569	585
1	152	147
2	72	40
3	69	65
4	263	191
5	65	27
7	82	101
8	338	319
9 K 0		
1	120	102
2	329	327
3	180	169
4	87	56
5	158	166
6	223	237
7	111	109
10 K 0		
5	60	26
6	162	162
0 K 1		
1	462	449
3	393	373
5	223	222
7	150	152
9	66	50
1 K 1		
0	569	537
1	345	335
3	356	357
4	298	287
5	467	476
7	262	267
8	143	140
2 K 1		
1	47	37
2	158	156
3	47	30
4	192	196
5	59	62
6	164	152
8	187	190
10	98	88
3 K 1		
0	387	375
1	442	434
4	258	253
5	110	105
7	185	183
8	138	124
10	66	83
11	152	165
4 K 1		
1	342	335
2	123	122
3	268	263
5	156	174
6	62	57
7	183	195
8	66	22
5 K 1		
0	244	247
1	475	475
3	156	171
4	256	256
5	56	55
7	209	215
8	88	56
9	286	276
6 K 1		
1	83	41
2	139	145
3	56	30
4	113	102
6	100	116
7	78	57
8	125	123
10	67	63
7 K 1		
0	123	135
1	186	200
3	186	194
4	160	162
5	280	285
6	116	116
7	208	208
9	66	38
8 K 1		
1	158	131
2	98	107
3	159	162
4	67	24
5	78	76
6	82	62
7	85	88
9 K 1		
1	77	60
3	264	259
4	85	77
5	251	257
6	63	28
7	95	93
10 K 1		
1	83	8
2	115	119
3	61	22
4	64	48
5	66	50
6	75	85
11 K 1		
1	172	152
2	80	70
3	119	139
2	659	700
4	386	375
6	419	425
8	192	181
10	380	369
1 K 2		
1	402	432
2	450	441
3	313	308
5	172	175
6	142	135
7	188	199
9	219	187
11	147	147
2 K 2		
1	451	444
3	211	205
4	929	949
5	468	474
6	103	102
7	56	5
8	184	194
9	312	313
10	63	55
3 K 2		
1	49	9
2	75	37
3	564	598
4	127	114
5	382	385
6	67	55
7	64	21
8	98	82
9	121	120
11	215	219
4 K 2		
0	744	732
1	77	56
2	514	515
3	52	52
4	547	574
6	524	531
8	237	245
9	83	76
10	162	139
5 K 2		
1	262	264
2	517	521
3	165	161
4	147	145
5	234	229
6	310	310
7	252	253
8	148	159
9	74	106
10	195	184
6 K 2		
0	549	548
2	53	13
3	78	81
4	366	371
8	292	290
9	78	65
7 K 2		
1	320	310
2	91	110
4	57	41
5	100	120
8 K 2		
0	97	62
2	351	351
5	165	156
6	278	285
9 K 2		
1	336	335
2	202	203
3	71	66
6	154	155
10 K 2		
0	214	212
1	59	52
3	92	91
4	278	284
11 K 2		
2	116	97
3	289	277
0 K 3		
5	148	150
7	194	208
9	105	85
11	68	79
1 K 3		
3	347	356
4	260	272
5	464	456
7	221	215
8	102	80
10	67	48
11	88	100
2 K 3		
2	134	136
3	92	94
4	163	150
6	144	122
8	156	159
10	74	71
3 K 3		
1	320	319
3	329	320
4	140	136
5	129	137
6	91	67
7	148	147
8	137	129
9	263	255
10	78	43
4 K 3		
1	160	169
2	61	63
3	228	226
5	163	165
6	57	29
7	118	104
8	78	25
9	57	5
5 K 3		
0	275	276
1	378	373
2	74	70
3	189	177
4	190	197
5	106	82
6	75	53
7	182	178
6 K 3		
2	173	159
3	65	41
4	98	92
6	142	120
7	65	59
8	104	117
7 K 3		
0	71	108
1	157	155
3	161	187
4	188	200
5	278	269
6	83	81
7	180	177
8 K 3		
1	153	159
2	103	122
3	106	124
4	61	14
6	69	78
9 K 3		
0	141	123
1	82	44
3	239	238
5	229	236
6	67	55
10 K 3		
2	91	77
4	65	38
0 K 4		
6	120	120
8	637	635
10	189	180
1 K 4		
5	252	246
6	174	175
7	204	195
8	111	131
9	98	103
10	88	82
2 K 4		
5	246	287
6	338	351
8	80	71
9	214	210
10	263	252
3 K 4		
3	67	91
4	55	16
5	114	123
6	189	193
7	222	234
9	101	120
10	75	77
4 K 4		
5	142	143
7	100	32
8	216	210
9	135	146
5 K 4		
3	74	79
4	81	71
7	157	166
8	103	64
9	132	141
6 K 4		
0	282	298
2	384	376
3	118	47
4	183	180
5	162	153
6	274	261
7	69	25
8	153	155
7 K 4		
2	73	68
3	429	423
4	68	66
5	239	230
7	136	148
8 K 4		
0	430	439
1	157	111
2	69	41
4	142	147
5	80	20
9 K 4		
2	271	255
3	136	124
5	97	126
10 K 4		
1	94	94
2	246	238
2 K 5		
8	119	129
3 K 5		
7	149	139
9	240	244
4 K 5		
6	88	51
7	178	175
8	74	11
5 K 5		
6	72	25
7	154	158
8	80	4
6 K 5		
5	88	26
7	84	36
7 K 5		
3	131	122
5	176	180
6	98	94
8 K 5		
3	126	117
4	66	23
5	75	65

Table 4b. Calculated and observed structure factors for andalusite at 12 kbar; step-scan data.

H	OBS	CALC
0 K 0		
0	0	3200
2	150	158
4	476	477
6	192	188
1 K 0		
1	440	416
2	394	393
3	229	253
4	150	152
5	354	353
6	259	261
7	273	282
8	172	180
2 K 0		
0	193	198
1	351	355
2	709	709
3	113	117
4	97	98
5	426	423
6	465	475
8	89	97
3 K 0		
1	503	502
2	698	652
3	164	144
5	192	187
6	294	299
7	333	326
9	171	168
4 K 0		
0	362	367
1	320	318
3	108	101
4	696	727
5	216	219
8	287	295
9	187	187
5 K 0		
1	469	473
2	176	177
3	140	128
4	101	99
6	111	102
7	243	242
8	123	86
9	197	204
0	438	441
1	254	263
2	533	511
4	296	287
5	204	210
6	362	363
8	211	199
9	221	226
10	291	291
7 K 0		
1	102	101
3	576	579
5	319	327
6	117	112
7	195	188
8	130	119
9	113	94
8 K 0		
0	574	593
1	153	144
4	175	196
7	127	113
8	349	345
9 K 0		
1	84	99
2	336	344
3	196	189
5	170	176
6	239	247
7	123	117
10 K 0		
6	190	170
0 K 1		
1	423	429
3	385	372
5	229	224
7	166	160
1 K 1		
0	517	505
1	321	327
3	351	352
4	294	287
5	472	474
7	276	282
8	147	142
2 K 1		
1	51	42
2	145	154
4	197	198
5	83	72
6	154	155
8	198	205
10	100	90
3 K 1		
0	370	369
3	365	349
4	254	254
5	117	112
7	194	193
8	134	132
9	252	333
10	70	83
11	185	180
4 K 1		
1	337	332
2	119	118
3	274	269
5	178	174
7	200	202
5 K 1		
0	260	254
1	478	472
3	175	170
4	263	269
7	228	228
8	86	65
9	289	294
6 K 1		
2	151	154
4	123	115
6	116	110
8	132	131
7 K 1		
0	151	135
1	195	200
3	212	208
4	165	169
5	285	293
6	131	129
7	226	210
8 K 1		
1	140	135
2	113	114
3	174	171
7	112	95
9 K 1		
0	216	217
1	77	61
3	263	264
4	91	85
5	268	269
7	104	107
10 K 1		
2	120	130
6	112	99
11 K 1		
1	143	162
3	136	139
0 K 2		
6	428	429
8	176	181
10	377	381
1 K 2		
1	390	422
2	458	435
3	311	310
5	178	177
6	148	148
7	206	204
9	219	199
10	87	90
11	145	152
1	445	437
3	212	210
4	925	909
5	473	472
6	110	97
8	193	194
9	318	322
3 K 2		
3	569	587
4	120	110
5	391	391
8	100	89
9	119	113
11	229	235
4 K 2		
0	741	711
1	89	67
2	503	510
4	549	573
6	539	541
8	253	257
9	128	81
10	160	154
5 K 2		
1	270	268
2	517	521
3	169	168
4	142	144
5	245	242
6	323	321
7	253	254
8	163	165
9	128	114
10	209	197
6 K 2		
0	550	557
4	385	375
8	298	307
7 K 2		
1	322	323
2	117	107
5	128	126
7	271	294
8 K 2		
0	75	60
6	299	298
9 K 2		
1	342	351
2	225	218
6	160	161
10 K 2		
0	224	222
3	106	98
4	306	302
2	124	112
3	298	299
0 K 3		
5	154	160
7	195	215
9	105	98
1 K 3		
3	349	361
4	272	275
5	466	455
7	221	219
8	96	83
11	122	117
2 K 3		
2	136	138
3	106	93
4	160	153
6	131	125
8	167	175
10	97	71
3 K 3		
1	309	323
3	327	320
4	142	140
5	136	139
6	88	70
7	159	149
8	141	137
9	265	270
4 K 3		
1	166	167
3	233	234
5	153	160
7	125	111
5 K 3		
0	282	278
1	375	374
3	184	180
4	210	207
5	93	86
7	187	184
8	105	103
9	234	238
6 K 3		
6	121	110
8	107	119
7 K 3		
0	124	103
1	144	152
3	204	204
4	199	205
5	271	280
6	113	85
7	181	173
8 K 3		
1	161	168
2	116	125
3	133	135
6	76	76
7	130	127
9 K 3		
0	126	135
3	254	246
5	259	251
6	94	62
10 K 3		
2	105	90
0 K 4		
6	120	126
8	653	663
10	200	188
1 K 4		
5	263	250
6	176	178
7	198	207
8	123	134
9	122	109
10	95	93
2 K 4		
5	302	300
6	345	364
9	219	221
10	279	275
3 K 4		
3	92	92
5	140	135
6	207	204
7	247	243
9	135	129
10	117	99
4 K 4		
4	572	564
5	149	149
8	227	227
9	168	159
5 K 4		
5	97	98
7	170	177
9	151	160
6 K 4		
0	297	303
2	395	387
4	196	199
5	152	154
6	277	275
8	156	170
7 K 4		
3	440	440
5	248	251
7	159	162
8 K 4		
0	440	449
1	103	105
4	159	161
9 K 4		
1	106	73
2	268	275
3	134	146
5	147	139
10 K 4		
1	96	96
2	252	253
2 K 5		
8	145	137
3 K 5		
7	156	155
9	250	259
4 K 5		
6	78	52
7	179	184
5 K 5		
7	173	173
6 K 5		
4	79	73
7 K 5		
3	151	131
4	82	64
5	185	187
6	124	109
8 K 5		
3	133	126

Table 4c. Calculated and observed structure factors for andalusite at 25 kbar; step-scan data.

H	OBS	CALC
H 0 0		
2	216	195
4	396	372
6	442	438
8	547	561
0	108	57
H 1 0		
1	476	420
2	370	356
3	530	502
4	337	319
5	468	461
6	254	253
7	87	105
8	147	132
0	126	109
1	123	114
H 2 0		
0	170	159
1	399	402
2	720	716
3	714	655
5	165	171
6	490	498
7	110	107
9	325	329
0	287	296
1	108	86
H 3 0		
1	222	246
2	112	116
3	202*	137
4	103	93
5	128	121
6	86	77
7	568	564
9	182	174
H 4 0		
0	497	470
1	143	147
2	93	96
4	702	716
5	93	98
6	260	268
7	97	88
8	175	188
H 5 0		
0	221	224
0	187*	73
6	192	188
9	178	155
H 6 0		
2	423	469
3	269	275
4	81	62
5	104	109
6	363	344
7	95	109
8	241*	12
9	210	217
10	177	159
H 7 0		
5	225	226
7	175	183
8	114	103
9	103	92
H 0 1		
1	512	511
3	371	372
5	250	247
7	155	132
9	196	201
H 1 1		
0	467	431
1	335	329
2	74	45
3	422	428
4	330	326
5	439	471
7	180	189
8	126	125
11	159	159
H 2 1		
1	110*	32
2	153	154
3	85	75
4	116	115
6	149	146
8	122	103
10	129	121
H 3 1		
0	383	364
1	353	357
3	344	341
4	258	264
5	167	171
7	202	206
8	148	154
H 4 1		
1	295	289
2	191	191
3	258	233
5	252	259
7	171	162
H 5 1		
0	232	227
1	468	467
3	110	107
4	171	167
7	282	287
8	110	84
9	249	246
H 6 1		
2	156	150
6	120	113
7	126	123
9	106	19
10	110	86
H 7 1		
0	163	164
1	250	264
3	189	194
4	187	184
5	217	209
7	215	203
9	138	99
H 8 1		
1	158	144
2	187	187
3	121	127
6	100	107
H 9 1		
3	295	318
5	261	271
H 0 2		
4	653	709
6	556	542
10	207	215
H 1 2		
1	411	430
2	432	438
5	267	266
7	322	311
9	329	327
H 2 2		
0	676	683
1	455	432
8	347	348
9	204	200
11	135	111
H 3 2		
1	316	313
2	213	208
3	566	589
5	161	164
6	109	80
10	121	96
H 4 2		
0	368	367
2	884	913
4	547	564
5	115	127
6	364	369
10	287	274
H 5 2		
1	157	167
2	445	458
3	373	383
5	216	231
8	155	159
10	133	102
H 6 2		
0	410	415
1	149	146
2	105	94
4	502	519
5	304	307
7	126	64
8	282	277
9	159	145
H 7 2		
1	200	201
5	241	239
7	273	274
9	235	240
H 8 2		
0	162	172
1	163*	39
2	194	191
4	239	245
5	155	165
6	292	277
8	123	22
H 9 2		
1	182	192
H 10 2		
0	362	360
2	124	38
4	170	144
5	168	172
H 0 3		
5	263	269
7	114	108
9	141	124
H 1 3		
3	231	313
4	174	166
5	365	372
7	143	144
8	129	151
H 2 3		
1	78	45
2	142	141
5	87	70
6	162	158
8	122	114
H 3 3		
0	307	297
1	348	355
2	91	83
3	309	312
4	213	227
5	176	175
7	196	196
8	115	118
9	239	233
H 4 3		
1	270	267
2	185	147
3	137	139
5	194	198
6	95	79
7	190	199
9	107	68
H 5 3		
0	143	160
1	437	447
3	137	142
4	154	156
7	270	272
9	219	229
H 6 3		
2	151	124
3	111	72
6	122	115
0	295	220
1	213	211
3	139	154
4	113	98
5	169	172
7	164	169
8	140	120
H 8 3		
2	179	158
3	120	130
5	143	95
6	122	102
H 9 3		
2	107	14
3	259	253
5	211	218
H 11 3		
1	119	103
H 2 4		
5	119	127
6	380	382
7	100	80
9	245	261
10	150	238
H 3 4		
2	110	95
3	94	102
5	93	97
6	98	57
7	414	432
9	132	136
H 4 4		
0	180	175
4	554	549
5	105	71
6	198	195
7	101	66
8	156	154
H 5 4		
1	263	262
2	286	287
3	145	139
4	142	151
6	149	139
7	221	239
9	186	124
H 6 4		
0	138	128
1	174	174
2	366	363
H 7 4		
1	207	200
3	244	243
5	171	175
7	132	149
H 8 4		
0	629	636
1	103	116
4	241	218
6	149	152
H 9 4		
1	118	101
2	205	199
3	142	123
4	145	141
5	133	152
H 10 4		
0	176	167
1	142	103
2	249	252
H 5 5		
2	109	88
5	111	20
7	159	177
H 6 5		
2	139	109
4	104	44
7	111	103
H 7 5		
1	196	192
3	148	147
4	176	173
5	166	153
H 8 5		
2	129	130
H 9 5		
3	256	238

Table 4d. Calculated and observed structure factors for andalusite at 37 kbar; continuous scan data.

H	OBS	CALC
H 0 0		
0	0	3200
2	204	201
4	377	373
6	448	441
8	597	595
10	69	49
H 1 0		
1	453	434
2	375	366
3	534	520
4	311	318
5	508	479
6	272	253
7	96	107
8	137	137
9	103	107
10	94	102
11	121	119
H 2 0		
0	155	147
1	407	410
2	733	734
3	720	683
4	48	17
5	173	173
6	517	518
7	113	103
9	304	335
10	324	318
11	105	75
H 3 0		
1	225	244
2	76	106
3	187	149
4	104	104
5	121	124
6	89	81
7	587	581
8	84	82
9	192	181
10	79	34
H 4 0		
0	496	482
4	751	742
6	262	274
7	74	94
8	197	202
H 5 0		
3	189	188
4	205	226
5	93	77
6	222	216
7	324	325
9	159	152
H 6 0		
0	168	172
1	254	252
2	508	505
3	283	285
4	56	60
5	116	106
6	355	359
7	86	89
8	74	24
9	244	241
H 6 0		
10	170	178
H 7 0		
1	282	290
2	71	48
3	326	321
5	224	228
7	183	176
8	96	115
9	99	111
H 8 0		
4	289	300
5	115	116
6	189	193
7	110	114
H 0 1		
1	504	527
3	384	381
5	259	269
6	63	0
7	144	148
9	208	212
11	96	92
H 1 1		
0	440	439
1	316	327
2	44	45
3	418	434
4	373	328
5	495	488
7	189	194
8	116	125
11	172	173
H 2 1		
1	40	41
2	138	148
4	93	116
6	142	139
8	116	121
10	126	125
11	83	65
H 3 1		
0	389	371
1	360	363
3	372	344
4	278	262
9	266	263
11	137	147
H 4 1		
1	370	291
3	259	265
5	278	266
6	110	105
7	133	159
9	103	92
H 5 1		
0	242	225
1	480	481
3	106	113
4	167	157
5	87	55
7	303	307
8	84	84
9	272	264
H 6 1		
2	133	142
4	68	62
6	108	108
7	120	117
8	82	79
H 7 1		
0	185	166
1	275	270
2	80	18
3	192	200
4	162	170
5	222	229
6	77	46
7	205	217
8	92	92
9	113	110
H 8 1		
1	124	144
2	193	202
3	129	127
6	120	127
7	82	56
H 9 1		
3	314	330
5	294	289
H 10 1		
2	87	81
3	101	74
4	72	27
6	98	60
H 0 2		
4	769	735
6	569	560
8	76	66
10	247	230
H 1 2		
1	413	439
2	440	452
4	71	56
9	360	345
10	71	57
H 2 2		
0	683	711
1	451	433
4	512	529
5	523	519
7	124	103
8	355	364
9	217	219
11	102	103
H 3 2		
1	329	317
3	599	601
4	87	62
5	168	169
6	84	77
9	79	66
10	96	92
H 4 2		
0	384	374
2	931	950
3	101	84
4	565	579
5	129	133
6	387	383
7	79	65
10	295	296
H 5 2		
1	182	167
2	470	478
3	393	400
5	227	226
7	120	135
8	150	151
10	118	122
H 6 2		
0	419	415
1	185	163
3	73	78
4	497	523
5	312	336
7	81	68
8	295	300
9	154	149
H 7 2		
1	205	199
5	255	261
7	287	279
9	251	253
H 8 2		
0	166	161
2	196	192
3	96	89
4	263	257
5	166	162
6	305	291
7	74	77
H 9 2		
1	209	206
5	109	121
7	78	73
H 10 2		
0	402	385
1	88	76
2	78	43
3	85	74
4	172	171
5	178	182
H 11 2		
1	151	159
3	228	223
H 0 3		
5	297	289
7	112	116
9	141	135
H 1 3		
3	312	324
4	159	166
5	401	385
6	68	5
7	141	142
8	155	163
9	70	47
H 2 3		
2	135	145
4	79	67
6	150	151
8	140	130
10	97	90
H 3 3		
0	280	290
1	357	366
2	87	74
3	284	315
4	246	238
5	172	175
7	206	207
8	115	120
9	234	246
10	78	59
H 4 3		
1	266	282
2	165	164
3	162	155
4	61	32
5	178	201
6	96	90
7	200	198
9	94	88
H 5 3		
0	170	166
1	468	452
3	140	130
4	130	145
6	74	68
7	291	289
8	74	62
9	243	249
2	133	121
6	130	114
7	78	74
8	88	91
H 7 3		
0	207	220
1	190	201
3	158	149
4	90	90
5	183	178
7	180	175
8	121	122
H 8 3		
1	88	86
2	160	178
3	138	136
5	118	106
6	132	113
H 9 3		
0	82	78
3	271	270
5	245	239
H 10 3		
3	76	41
H 11 3		
0	82	53
1	122	124
H 1 4		
7	68	77
8	86	104
9	91	83
10	92	88
H 2 4		
5	150	143
6	405	390
7	77	79
9	270	270
10	241	252
H 3 4		
3	93	97
4	56	56
5	95	91
6	66	64
7	443	448
9	138	143
H 4 4		
1	66	93
2	76	55
4	589	571
5	91	73
6	185	196
7	72	73
8	164	157
H 5 4		
1	270	265
2	304	300
7	251	255
H 6 4		
0	104	129
1	182	180
2	392	380
3	191	188
5	95	88
6	276	273
7	85	69
H 7 4		
1	198	210
3	256	248
5	177	178
7	161	152
H 8 4		
0	652	666
1	96	110
2	93	78
4	234	229
5	92	93
6	163	156
H 9 4		
1	96	107
2	222	224
3	132	124
4	154	157
5	168	164
H 10 4		
0	164	166
1	107	117
2	258	255
H 4 5		
7	94	67
H 5 5		
4	97	86
6	72	41
7	195	195
H 6 5		
2	118	110
4	78	52
5	81	26
7	115	109
H 7 5		
0	68	61
1	190	198
2	83	21
3	167	156
4	163	170
5	167	173
H 8 5		
1	136	133
2	135	142
3	70	71
H 9 5		
3	253	251