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Complex Cubic A_6B Compounds. I. The Crystal Structure of Na_6Tl*

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Na_6Tl represents one of the two structure types so far found for complex A_6B compounds of cubic symmetry containing about 400 atoms each per smallest unit cube, arranged according to space group $F\bar{4}3m$. A complete structure determination has been carried out for this compound, with the use of packing maps and subsequent least-squares refinements employing intensity data of 1602 reflections measured with an automated X-ray diffractometer. The length of the cube edge is $a_o = 24{\cdot}154 \pm 0{\cdot}001$ Å (Cu $K\alpha_1 = 1{\cdot}54051$ Å) giving a calculated density of $\varrho_c = 2{\cdot}302$ g.cm^{-3}. The final R value is 0·137. This unit cube contains one formula unit of $Na_{352}Tl_{56}$ (or eight units of $Na_{44}Tl_7$) and the atoms are distributed among 15 different point sets. Because of the likelihood of variable composition, especially in possible isostructural compounds, it seems practical to retain the formula Na_6Tl as a name for this structure type. The basic building block of the structure consists of a complex of 14 icosahedra and 42 pentagonal prisms, which is nearly identical to one of the four complexes occurring in Cu_4Cd_3. Four such complexes share a Laves–Friauf polyhedron, the center of which was not fully occupied in the crystal used. Each thallium atom is surrounded by an icosahedron of sodium atoms in such a way that there are no Tl–Tl contacts as was predicted on the basis of magnetic measurements.

Introduction

The crystal structure study of Na_6Tl reported here was proposed to us by Professor J. F. Smith (Department of Metallurgy, Iowa State University) for the purpose of supplementing the results, obtained at his laboratory from measurements of magnetic susceptibilities. These were found to be temperature-dependent paramagnetic and of the Curie–Weiss type, giving a Curie constant of $(4{\cdot}92 \pm 0{\cdot}25) \times 10^{-2}$ e.m.u., (°K/g.f.w.), which corresponds to $0{\cdot}63 \pm 0{\cdot}02$ Bohr magnetons per formula unit of Na_6Tl (*i.e.* per Tl atom). On the basis of this result and other calculations, Greiner, Hansen, & Smith (1969) predicted that the thallium atoms in Na_6Tl are isolated from one another, implying a Tl–Tl internuclear separation of about 5 Å or more.

A complete crystal-structure determination (R = 16%) confirming the above prediction was carried out here, during the summer of 1967, with the use of X-ray data obtained from an irregular crystal at the Ames Laboratory. The results were reported to that laboratory, and an outline of some of the structural features together with the magnetic data was given by Greiner *et al.* (1969). The structure is cubic, space group $F\bar{4}3m$, $a_o = 24{\cdot}154$ Å.

The refinement of the structural parameters, and hence the present final report, was delayed to await the collection of improved X-ray data from a spherically ground crystal and the development of facilities for sphere grinding of the extremely reactive compound.

Earlier investigations establishing the existence of Na_6Tl, but providing no crystallographic data, were those of Kurnakow & Pushin (1902) and Grube & Schmidt (1936). The two papers present almost identical results, stating that the compound forms peritectically at 85·9 at.% sodium ($Na_{6{\cdot}1}Tl$) and 78 °C.

Experimental

Sample preparation

A 10-gram sample of Na_6Tl (12·1 at.% Tl) was prepared by melting together reagent grade sodium (Fisher Scientific Company) and thallium of 99·99% purity (United Mineral and Chemical Corporation) in a stainless steel crucible, which was loaded and hermetically sealed by arc welding under dry argon gas. The sample was heated for one day at 350 °C and frequently agitated, then annealed inside an oil bath for two days at $70{\cdot}0 \pm 0{\cdot}5$ °C, for two days at $66.0 \pm 0{\cdot}5$ °C, and finally cooled to room temperature at a rate of about 3° per hour.

The crucible was opened inside a locally designed and constructed glove box, equipped with a sphere grinder and a continuously operating, very effective NaK ('nack') gettering device, thus allowing ample time to manipulate the extremely reactive single crystals without causing detectable corrosion. Details of the apparatus will be described elsewhere.

Because Na_6Tl is soft, spheres were obtained within a few minutes of grinding. These were encapsulated in glass capillaries according to the description given by

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Hansen (1968), thus avoiding the use of oil for corrosion protection.

Unit cell and space group

Laue, rotation, and Weissenberg photographs of layer lines 0 to 4 about [001] obtained with the use of an encapsulated sphere showed that the structure was face-centered cubic having Laue symmetry *m*3*m*. Only reflections of the type *hkl*: *h*+*k*, *k*+*l*, (*l*+*h*)=2*n* were present. The probable space group is, accordingly, *F*432, *Fm*3*m* or *F*$\bar{4}$3*m*.

The length of the cube edge had been determined earlier at the Ames Laboratory with the use of an irregular crystal fragment, a General Electric diffractometer equipped with a 0·02° detector slit and a copper-target X-ray tube. Half-height, 2θ values were

Table 1. *Observed and calculated structure factors for* Na$_6$Tl

Each group of four columns contains, from left to right, indices *l*, observed structure factors, calculated structure factors, and standard deviations. Two dashes indicate that the measured value was given zero weight. Values of *F*(cal) are based on the final isotropic refinement (Table 2).

0	0	L	
0	0	8267	--
2	745	749	--
4	670	668	4
6	1536	1530	7
8	141	150	27
10	902	921	6
12	2419	2439	11
14	296	259	19
16	588	526	12
18	1140	1147	8
20	721	745	12
22	274	328	30
24	429	447	22
26	240	221	39
28	67	18	93
30	590	526	20
32	73	76	101
34	122	27	81
36	35	90	136
38	0	10	--
0	2	L	
2	531	450	--
4	0	5	--
6	79	15	36
8	799	793	6
10	170	216	25
12	325	281	16
14	216	252	26
16	132	71	44
18	320	266	23
20	324	354	25
22	163	157	46
24	0	80	--
26	0	51	--
28	0	26	--
30	97	44	82
32	98	81	67
34	17	8	146
36	106	26	90
38	0	38	--
0	4	L	
4	766	761	--
6	649	622	7
8	14	4	81
10	598	578	9
12	0	51	--
14	670	692	10
16	632	667	12
18	157	138	42
20	93	90	65
22	229	137	36
24	234	173	37
26	255	265	37
28	38	9	114
30	0	137	--
32	25	6	134
34	41	52	126
36	0	64	--
38	135	27	82
0	6	L	
6	3715	3742	11
8	102	210	38
10	586	577	9
12	1319	1352	7
14	413	441	16
16	300	404	23
18	1046	1059	9
20	352	332	24
22	194	164	41
24	802	784	13
26	222	229	41
28	0	70	--
30	194	199	53
32	62	71	107
34	0	57	--
36	244	203	52
38	13	10	158
0	8	L	
8	783	760	7
10	248	312	21
12	263	247	23
14	74	168	64
16	49	60	82
18	138	92	48
20	213	258	37
22	78	73	77
24	76	20	82
26	19	75	126
28	37	93	117
30	50	41	113
32	2	89	158
34	102	14	92
36	153	32	76
38	39	30	138
0	10	L	
10	1600	1606	8
12	465	492	15
14	291	247	24
16	433	367	18
18	40	45	94
20	527	535	17
22	55	193	91
24	0	95	--
26	156	65	57
28	0	2	--
30	177	168	60
32	176	102	62
34	0	62	--
36	80	74	108
0	12	L	
12	1697	1663	8
14	224	172	31
16	175	134	41
18	913	896	11
20	156	104	50
22	0	100	--
24	469	478	22
26	33	69	118
28	0	29	--
30	321	301	37
32	0	17	--
34	0	12	--
36	0	87	--
0	14	L	
14	351	426	23
16	299	318	27
18	0	47	--
20	17	72	121
22	38	45	107
24	0	117	--
26	165	233	59
28	4	8	151
30	63	97	111
32	7	10	158
34	0	48	--
36	63	45	121
0	16	L	
16	401	457	22
18	0	82	--
20	188	150	46
22	227	106	41
24	86	132	86
26	172	172	58
28	49	9	116
30	111	91	85
32	11	19	154
34	0	38	--
0	18	L	
18	786	785	14
20	0	37	--
22	0	45	--
24	344	306	32
26	0	51	--
28	3	16	157
30	212	191	56
32	0	3	--
34	46	1	131
0	20	L	
20	312	363	34
22	91	119	85
24	147	122	67
26	73	44	133
28	0	16	--
30	10	90	157
32	0	80	--
0	22	L	
22	78	64	96
24	3	35	155
26	86	28	98
28	118	0	85
30	4	34	166
32	51	29	130
0	24	L	
24	243	271	49
26	0	60	--
28	28	0	142
30	31	59	145
0	26	L	
26	89	122	100
28	10	9	160
1	1	L	
1	584	549	--
3	642	665	--
5	1387	1382	6
7	1022	1043	6
9	641	597	8
11	653	680	8
13	696	717	9
15	431	504	15
17	431	422	17
19	379	377	21
21	350	224	23
23	363	375	24
25	445	397	22
27	100	122	73
29	68	87	96
31	0	90	--
33	14	67	146
35	129	109	80
37	115	101	88
39	79	13	111
1	3	L	
3	1457	1440	6
5	17	28	66
7	142	178	27
9	1174	1169	6
11	387	381	13
13	232	215	23
15	809	764	9
17	298	277	23
19	309	268	25
21	413	365	21
23	213	202	39
25	19	10	121
27	356	297	28
29	111	119	75
31	126	84	74
33	145	130	71
35	0	13	--
37	32	38	138
1	5	L	
5	549	542	7
7	1019	1007	6
9	639	667	8
11	1081	1079	6
13	346	385	17
15	479	394	14
17	383	408	19
19	664	646	13
21	323	367	26
23	103	168	66
25	183	180	48
27	49	36	103
29	186	199	53
31	242	221	65
33	76	25	101
35	37	83	132
37	0	43	170
1	7	L	
7	548	548	9
9	357	383	14
11	526	565	11
13	759	725	9
15	69	71	67
17	503	513	16
19	456	416	18
21	60	193	85
23	70	68	82
25	230	192	40
27	141	127	62
29	241	192	43
31	142	187	70
33	0	64	--
35	0	42	--
37	0	16	--
1	9	L	
9	1082	1092	6
11	392	351	15
13	347	357	19
15	419	372	17
17	178	188	40
19	253	253	31
21	431	579	15
23	115	160	64
25	289	233	34
27	165	156	56
29	54	57	108
31	0	53	--
33	102	109	90
35	95	64	97
37	70	42	110
1	11	L	
11	438	471	15
13	825	809	10
15	425	420	15
17	462	474	18
19	181	154	43
21	183	139	45
23	121	151	65
25	335	322	30
27	90	134	84
29	74	114	96
31	97	93	90
33	70	34	107
35	176	78	67
37	0	52	--
1	13	L	
13	469	448	16
15	0	28	--
17	60	80	83
19	452	442	20
21	87	173	75
23	275	278	34
25	126	169	68
27	39	87	117
29	20	52	136
31	82	86	98
33	71	75	130
35	67	52	113
1	15	L	
15	703	676	13
17	31	9	134
19	297	301	30
21	169	83	51
23	0	24	--
25	169	122	56
27	271	226	41
29	0	91	--
31	141	110	74
33	161	73	71
35	0	43	--
1	17	L	
17	0	41	--
19	365	340	26
21	169	159	53
23	143	208	62
25	97	89	84
27	4	54	151
29	113	55	82
31	62	76	114
33	0	50	--
35	0	39	--
1	19	L	
19	104	104	73
21	12	72	136
23	0	69	--
25	165	186	61
27	33	83	130
29	0	90	--
31	11	63	157
33	64	33	118
1	21	L	
21	368	294	30
23	36	65	123
25	144	133	69
27	0	62	--
29	0	42	--
31	0	35	--
1	23	L	
23	63	44	109
25	156	87	69
27	5	56	160
29	15	75	151
31	0	53	--
1	25	L	
25	0	61	--
27	70	12	111
29	29	58	143
1	27	L	
27	0	70	--
2	2	L	
2	966	963	5
4	1606	1581	7
6	469	447	8
8	2267	2309	10
10	582	581	9
12	677	689	9
14	607	629	11
16	634	615	12
18	520	517	15
20	513	514	16
22	678	654	14
24	227	181	38
26	184	241	48
28	169	155	50
30	178	104	55
32	4	82	153
34	153	162	73
36	0	40	--
38	21	99	150
2	4	L	
4	712	667	--
6	222	246	18
8	959	988	6
10	932	941	6
12	430	476	13
14	1107	1134	7
16	771	765	10
18	201	190	35
20	397	455	21
22	383	390	23
24	226	206	38
26	75	141	86
28	338	311	31
30	16	11	138
32	189	166	57
34	70	53	107
36	0	38	--
38	35	30	138
2	6	L	
6	772	794	6
8	357	347	13
10	168	122	27
12	134	134	37
14	467	476	14
16	262	297	25
18	249	227	32
20	90	128	67
22	214	179	35
24	215	163	41
26	107	166	71
28	53	109	103
30	34	43	123
32	4	63	153
34	27	45	137
36	0	22	--
38	0	42	--
2	8	L	
8	607	603	9
10	733	745	8
12	696	672	10
14	1022	1024	9
16	632	642	13
18	478	496	17
20	0	155	--
22	275	243	32
24	250	227	36
26	209	173	44
28	350	330	31
30	134	65	71
32	159	163	67
34	67	63	111
36	2	15	165
38	59	46	124
2	10	L	
10	735	[illegible]	9
12	206	213	36
14	656	674	12
16	620	659	13
18	243	212	32
20	324	356	26
22	337	336	27
24	0	49	--
26	226	232	44
28	119	155	73
30	90	77	89
32	131	66	76
34	65	103	112
36	0	18	--
2	12	L	
12	636	609	12
14	256	250	28
16	171	117	42
18	389	375	22
20	252	220	34
22	219	247	40
24	66	124	92
26	55	107	102
28	110	146	78
30	17	41	141
32	55	96	116
34	18	64	150
36	0	22	--
2	14	L	
14	200	184	36
16	295	266	27
18	333	270	26
20	327	339	28
22	381	376	26
24	162	150	56
26	60	141	102
28	30	93	125
30	21	41	140
32	0	68	--
34	58	92	119
36	61	40	122
2	16	L	
16	273	252	31
18	185	188	45
20	339	316	28
22	339	328	30
24	21	71	129
26	128	157	71
28	91	98	91
30	0	31	--
32	23	61	143
34	91	87	102
2	18	L	
18	273	243	35
20	182	141	50
22	107	159	75
24	75	127	93
26	0	67	--
28	133	128	75
30	0	22	--
32	0	82	--
34	15	42	159
2	20	L	
20	132	107	66
22	21	116	132
24	0	40	--
26	151	128	69
28	35	91	131
30	97	54	96
32	55	42	123
2	22	L	
22	0	95	--
24	142	98	72
26	39	81	127
28	137	157	79
30	0	18	--
32	124	85	89
2	24	L	
24	63	56	111
26	8	72	157
28	74	44	112
30	0	24	--
2	26	L	
26	0	23	--
28	48	71	129
3	3	L	
3	1092	1072	5
5	987	1007	5
7	1648	1606	8
9	670	707	8
11	1146	1170	6
13	1223	1253	6
15	0	94	--
17	827	629	19
19	579	628	15
21	142	197	51
23	472	513	27
25	148	268	55
27	206	216	46
29	214	255	47
31	37	135	122
33	0	127	--
35	0	91	--
37	25	76	144
3	5	L	
5	325	326	13
7	539	483	9
9	1061	1099	6
11	0	29	--
13	508	484	12
15	623	570	12
17	199	161	34
19	134	52	43
21	543	495	16
23	198	146	44
25	118	136	65
27	220	185	44
29	60	13	103
31	0	6	--
33	63	95	109
35	31	39	137
37	12	31	141
3	7	L	
7	746	738	7
9	1096	1086	6
11	301	296	19
13	590	572	11
15	617	592	12
17	451	464	17
19	245	245	32
21	469	436	19
23	340	313	27
25	168	144	51
27	282	272	36
29	30	113	124
31	39	57	123
33	135	147	76
35	68	36	110
37	0	60	--
3	9	L	
9	379	285	17
11	765	757	9
13	768	783	10
15	348	406	19
17	674	705	13
19	478	507	18
21	142	150	53
23	378	392	25
25	207	256	44
27	97	145	79
29	130	178	71
31	0	79	--
33	0	78	--
35	94	112	98
37	0	64	--
3	11	L	
11	368	363	19
13	357	321	20
15	685	667	12
17	127	142	53
19	276	265	30
21	322	284	28
23	133	117	59
25	0	25	--
27	270	232	39
29	49	73	115
31	67	67	119
33	207	107	57
35	45	15	128
37	14	23	160
3	13	L	
13	511	509	15
15	378	398	21
17	411	386	21
19	262	262	32
21	326	313	29
23	232	234	41
25	109	122	76
27	260	214	42
29	54	101	112
31	51	55	119
33	229	123	57
35	0	29	--
3	15	L	
15	92	88	67
17	373	345	24
19	255	327	34
21	134	148	61
23	167	215	54
25	0	99	--
27	0	36	--
29	43	169	122
31	143	99	73
33	74	25	109
35	0	50	--
3	17	L	
17	272	245	32
19	181	173	49
21	312	296	32
23	144	184	63
25	91	72	87
27	89	177	92
29	157	77	69
31	0	25	--
33	79	94	108
35	20	23	154
3	19	L	
19	178	181	51
21	68	152	94
23	150	120	66
25	4	18	151
27	66	160	107
29	0	66	--
31	0	43	--
33	70	69	114
3	21	L	
21	8	28	143
23	100	175	86
25	66	126	107
27	36	31	130
29	56	86	120
31	0	28	--
3	23	L	
23	21	160	140
25	98	47	91
27	25	118	141
29	83	65	133
31	0	22	--
3	25	L	
25	140	48	76
27	0	43	--
29	11	12	162
3	27	L	
27	27	45	109
4	4	L	
4	1418	1381	7
6	870	849	6
8	1453	1451	7
10	749	755	8
12	217	155	24
14	1192	1075	7
16	910	922	9
18	297	300	25
20	420	438	20
22	397	437	22
24	17	88	121
26	377	354	27
28	178	171	53
30	209	140	50
32	47	33	117
34	119	152	82
36	0	43	--
38	0	64	--
4	6	L	
6	422	463	11
8	596	616	9
10	669	647	9
12	516	515	12
14	0	93	--
16	424	360	18
18	255	200	29
20	328	402	21
22	157	165	49
24	145	147	56
26	0	59	--
28	51	71	134
30	123	120	73
32	0	93	--
34	0	51	--
36	7	57	160
38	0	31	--
4	8	L	
8	1273	1256	6
10	800	775	8
12	199	168	29
14	311	320	22
16	382	383	20
18	334	308	24
20	429	439	20
22	425	512	18
24	216	162	42
26	180	187	51
28	69	119	95
30	64	50	134
32	134	87	74
34	181	119	64
36	117	42	89
4	10	L	
10	1059	1068	7
12	169	177	36
14	561	556	16
16	390	433	20
18	103	110	62
20	595	596	16
22	459	452	21
24	237	193	39
26	183	122	51
28	146	179	64
30	0	92	--
32	148	129	70
34	0	64	--
36	99	66	98
4	12	L	
12	127	136	48
14	344	329	22
16	170	220	43
18	237	212	34
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34	68	36	112
36	132	19	83
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16	650	631	14
18	160	187	49
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22	85	126	81
24	45	139	107
26	253	227	41
28	219	184	49
30	93	95	92
32	23	71	143
34	107	78	94
36	2	21	171
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18	119	90	63
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22	109	113	74
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26	133	93	73
28	15	62	145
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32	25	72	147
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24	119	42	90
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26	43	19	139
28	95	44	97
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4	26	L	
26	43	98	133
28	109	31	95
5	5	L	
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9	456	453	11
11	487	523	12
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17	562	541	15
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23	311	328	29
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33	72	22	103
35	89	126	100
37	0	82	--
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9	31	76	76
11	540	572	11
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17	357	361	22
19	241	269	32
21	63	33	84
23	228	229	38
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27	48	83	107
29	22	94	133
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33	78	47	102
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29	66	148	103
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27	79	78	93
29	81	68	96
31	72	89	106
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17	208	202	40
19	140	148	56
21	504	477	21
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25	301	270	36
27	93	66	88
29	66	63	107
31	72	63	105
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35	60	79	120
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19	172	149	50
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25	185	176	55
27	62	62	107
29	95	59	98
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19	292	277	34
21	143	189	63
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31	108	101	91
33	78	18	112
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14	408	362	17
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22	140	243	53
24	444	456	22
26	199	167	46
28	41	52	114
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38	0	22	--
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16	220	245	32
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22	132	114	57
24	93	99	80
26	156	177	57
28	39	92	117
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12	40	125	84
14	489	463	16
16	505	537	16
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20	149	139	52
22	196	120	44
24	158	150	56
26	159	211	59
28	7	17	146
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32	17	14	146
34	0	45	--
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14	170	193	41
16	256	325	31
18	825	879	11
20	122	95	61
22	65	95	89
24	527	457	20
26	133	66	67
28	118	87	75
30	226	201	51
32	46	57	124
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26	63	65	115
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17	236	262	32
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23	453	452	21
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37	0	100	--
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15	562	563	14
17	290	265	27
19	220	251	36
21	363	282	29
23	53	144	97
25	19	26	126
27	245	235	36
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23	265	260	36
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23	48	111	103
25	215	205	46
27	209	155	52
29	157	177	65
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33	29	80	140
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17	69	107	84
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27	68	103	102
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31	14	76	154
33	65	58	117
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21	149	130	62
23	214	224	50
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29	118	44	85
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23	135	176	74
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25	132	93	81
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27	30	60	146
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18	444	421	19
20	364	372	23
22	473	466	21
24	163	177	53
26	159	176	59
28	85	132	90
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18	350	297	25
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22	218	209	42
24	93	141	79
26	111	85	76
28	143	142	68
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22	176	136	58
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28	63	62	120
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23	272	302	35
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29	244	245	46
31	126	156	77
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13	256	273	29
15	272	233	29
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19	63	123	87
21	533	485	19
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25	147	178	62
27	197	133	57
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23	236	242	43
25	219	267	48
27	47	59	117
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26	316	286	34
28	84	168	93
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22	263	268	36
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26	59	95	109
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22	26	108	135
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26	64	76	115
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23	179	219	52
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26	26	83	135
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22	48	48	117
24	0	46	--
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28	75	28	108
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22	0	81	--
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28	76	69	110
12	24	L	
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26	0	24	--
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26	0	55	--
13	13	L	
13	257	267	32
15	120	180	61
17	125	157	62
19	355	346	28
21	150	146	59
23	369	332	31
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27	69	116	92
29	56	35	116
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33	43	74	132
13	15	L	
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13	17	L	
17	58	116	97
19	291	266	36
21	69	72	97
23	158	216	63
25	43	85	122
27	94	84	93
29	8	21	157
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19	113	113	75
21	37	79	123
23	4	52	153
25	128	96	78
27	76	69	135
29	115	98	88
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27	71	69	[illegible]
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27	125	22	88
14	14	L	
14	405	410	23
16	354	366	25
18	233	189	40
20	[illegible]	[illegible]	[illegible]
22	172	172	57
24	37	38	[illegible]
26	198	156	55
28	43	61	125
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14	16	L	
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20	61	114	100
22	203	188	51
24	62	45	96
26	108	156	87
28	45	61	127
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20	55	62	107
22	74	[illegible]	[illegible]
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28	91	68	99
30	95	16	100
14	20	L	
20	140	201	71
22	135	142	74
24	80	104	121
26	108	45	89
28	0	61	--
30	0	21	--
14	22	L	
22	121	93	81
24	85	73	100
26	0	21	--
28	20	96	152
14	24	L	
24	0	67	--
26	0	16	--
15	15	L	
15	269	274	35
17	131	163	63
19	307	309	34
21	77	160	92
23	145	150	67
25	28	37	134
27	0	55	--
29	188	151	64
31	75	114	111
15	17	L	
17	83	73	86
19	42	15	113
21	216	226	50
23	0	31	--
25	31	76	132
27	48	[illegible]	[illegible]
29	0	18	--
31	17	13	153
15	19	L	
19	159	132	62
21	0	24	--
23	0	28	--
25	26	[illegible]	[illegible]
27	[illegible]	[illegible]	[illegible]
29	36	44	[illegible]
15	21	L	
21	6	[illegible]	[illegible]
23	0	[illegible]	--
25	[illegible]	144	[illegible]
27	0	33	--
29	0	22	--
15	23	L	
23	0	24	--
25	0	23	--
27	32	53	141
15	25	L	
25	0	87	--
16	16	L	
16	402	398	26
18	0	76	--
20	0	132	--
22	99	159	85
24	112	[illegible]	[illegible]
26	99	149	91
28	56	73	118
30	0	61	--
16	18	L	
18	41	[illegible]	[illegible]
20	0	20	--
22	75	36	99
24	119	48	87
26	103	41	91
28	0	46	--
30	0	15	--
16	20	L	
20	212	199	53
22	171	131	64
24	68	[illegible]	[illegible]
26	0	45	--
28	34	68	[illegible]
16	22	L	
22	58	[illegible]	116
24	0	44	--
26	0	37	--
16	24	L	
24	93	37	[illegible]
26	0	21	--
17	17	L	
17	82	[illegible]	[illegible]
19	119	[illegible]	[illegible]
21	0	[illegible]	--
23	129	[illegible]	[illegible]
25	16	64	147
27	51	42	[illegible]
29	0	17	--
17	19	L	
19	96	[illegible]	[illegible]
21	51	72	117
23	0	29	--
25	49	63	123
27	127	47	96
29	77	67	[illegible]
17	21	L	
21	0	[illegible]	--
23	0	34	--
25	123	[illegible]	[illegible]
27	0	[illegible]	--
17	23	L	
23	66	40	[illegible]
25	93	53	[illegible]
18	18	L	
18	122	122	[illegible]
20	63	[illegible]	[illegible]
22	121	113	79
24	231	188	51
26	0	33	--
28	82	69	[illegible]
18	20	L	
20	93	74	92
22	112	44	85
24	0	18	--
26	0	22	--
28	0	12	--
18	22	L	
22	41	82	[illegible]
24	48	47	[illegible]
26	4	26	[illegible]
18	24	L	
24	0	115	--
19	19	L	
19	44	127	121
21	60	47	113
23	0	115	--
25	60	86	[illegible]
27	95	36	[illegible]
19	21	L	
21	66	129	111
23	0	39	--
25	0	60	--
19	23	L	
23	145	86	79
25	0	29	--
20	20	L	
20	0	81	--
22	42	44	[illegible]
24	0	19	--
26	0	91	--
20	22	L	
22	19	72	149
24	29	12	149
21	21	L	
21	2	59	165
23	0	63	--
25	0	11	--
21	23	L	
23	0	39	--
22	22	L	
22	89	[illegible]	[illegible]

determined for 20 α_1 reflections in the region $142° \le 2\theta \le 161°$ with the 2θ-scan technique. The averages of these were fitted by least-squares calculations to the Nelson–Riley (1954) function and gave $a_0 = 24{\cdot}154 \pm 0{\cdot}001$ Å [$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051$ Å].

The extreme reactivity of Na_6Tl precluded experimental determination of the density. The unit-cell content was estimated with the use of average atomic volumes assuming a contraction of 10%. Assumption of 239 $Å^3$ per formula unit of Na_6Tl leads to a unit-cell content of approximately 412 atoms.

Intensity data

Intensities were measured on a locally assembled, Syntex-automated, E&A full-circle diffractometer, equipped with a scintillation detector modified according to Samson (1966), an Ortec counter circuitry with pulse-height analyser, a graphite monochromator designed and built in this laboratory's instrument shop, and a molybdenum-target X-ray tube. The diffractometer was aligned according to Samson (1967*a*). The X-ray collimator and the counter apertures were designed locally so as to provide maximum signal-to-background ratios.

The $2\theta:\theta$-scan method was used throughout at scanning speeds proportional to the peak intensities between 200 and 1500 counts per sec. The scanning speed used at, or below, 200 cps (peak counts) was $0{\cdot}5°\ \text{min}^{-1}$ and at, or above, 1500 cps $2°\ \text{min}^{-1}$. The total background counting time for each reflection was equal to the scanning time. This variable-scan-speed program was written by Dr Richard Stanford for the online Varian 620i computer controlling the diffractometer. This is the same principle now applied in a refined fashion to the well-known Syntex diffractometer.

The counter-aperture-to-crystal distance was set so as to give an optimal signal-to-background ratio, which was established by plotting the distance against the ratio. At the optimal setting of 3·25 inches the ratio was improved by a factor of four as compared to that obtained at the distance of about 1·25 inches (or less) used on certain unmodified commercial instruments. The locally designed X-ray tube holder used here provides for both horizontal and vertical tube alignment. In the present experiment, the X-ray tube was set vertically, and the plane-normal of the graphite monochromator was perpendicular to the diffraction vector.

The crystal used was a sphere of 0·117 mm radius. Spherical absorption-correction factors for $\mu R = 1{\cdot}84$ were applied to the measured intensities, and the effect of the monochromator on the polarization was taken into account with the use of the formula given by Arndt & Willis (1966), inserting $\theta_M = 6{\cdot}08°$ and $\epsilon = 90°$. 1602 symmetrically independent reflections were measured, of which as many as 989 had an integrated intensity which was less than, or equal to, one standard deviation. The large number of very weak reflections is due to the high temperature factor associated with the low-melting point and the softness of the compound. Some very low-order reflections were feared to be affected by air scattering because of their proximity to the primary beam and were given zero weight. All other F_o values marked in Table 1 by two dashes were given zero weight because the integrated intensity was either zero or negative.

Derivation and isotropic refinement of the structure

The structure was derived by the method outlined by Samson (1964) which employs packing maps of the 'most useful planes', the nature of which depends on the space group. Since the crystal of Na_6Tl was assumed (and soon found) to have the space-group symmetry $F\bar{4}3m$, many of the arguments used to determine its atomic arrangement are the same as those in the case of Cu_4Cd_3 (Samson, 1967*b*), and the reader is

Table 2. *The refined positional parameters* ($\times 10^5$), *population factors, and isotropic temperature factors for* Na_6Tl

The standard deviations are given in parentheses.

Atom no.	Kind	Point set	x	z	B
1	Na	48(*h*) *xxz*, *etc.*	14228 (14)	03346 (21)	5·7 (2) $Å^2$
2	Na	48(*h*) *xxz*, *etc.*	08984 (17)	26791 (20)	6·3 (2)
3	Na	48(*h*) *xxz*, *etc.*	15395 (16)	52856 (19)	6·4 (3)
4	Na	48(*h*) *xxz*, *etc.*	05604 (15)	76942 (21)	5·9 (2)
5	Na	48(*h*) *xxz*, *etc.*	19809 (14)	90985 (20)	5·9 (2)
6	Na	24(*f*) *x*00, *etc.*	10858 (28)		5·2 (3)
7	Tl	24(*f*) *x*00, *etc.*	33516 (4)		4·39 (4)
8	Na*	24(*g*) $x\frac{1}{4}\frac{1}{4}$, *etc.*	06815 (43)		7·3 (6)
9	Na	16(*e*) *xxx*, *etc.*	30267 (23)		4·1 (4)
10	Na	16(*e*) *xxx*, *etc.*	41542 (26)		3·4 (4)
11	Na	16(*e*) *xxx*, *etc.*	55549 (24)		3·6 (3)
12	Na	16(*e*) *xxx*, *etc.*	67234 (24)		3·6 (3)
13	Tl	16(*e*) *xxx*, *etc.*	16755 (3)		3·59 (4)
14	Tl	16(*e*) *xxx*, *etc.*	90136 (3)		3·30 (3)
15	Void†	4(*d*) $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, *etc.*			

* Occupancy 94 ± 2%.

† Occupancy 19 ± 5% if B is assumed to be 5·0.

referred to that paper for more details. Space group $F\bar{4}3m$ has a single most useful plane: the (110) plane.

An enlightening feature discovered in the course of this work was the ease with which the Patterson vectors could be interpreted when they were plotted on a transparent template and then superimposed on the packing map. In such a manner, the only reasonable interpretation of the *uuw* Patterson section of Na_6Tl was that the thallium atoms are located at the points marked 7, 13, and 14 on the (110) packing map shown in Fig. 1. It is seen that these points are arranged approximately around a fivefold axis of symmetry. Since the thallium atoms are smaller in radius (by about 10%) than the sodium atoms, it suggested itself that each of these represents the center of an icosahedron. Hence, the basic building block of the structure of Na_6Tl should incorporate a set of five icosahedra arranged about a fivefold axis of symmetry in a manner similar to that observed for one of the four atom complexes occurring in Cu_4Cd_3. Accordingly, the five polygonal sections through the icosahedra marked 7, 13, and 14 in Fig. 1 were placed so as to match the pattern created by the polygonal sections marked 20, 27, and 28 in Fig. 1 of Samson's (1967*b*) paper on Cu_4Cd_3. The perfect geometrical fit of the fivefold sets on the packing map aroused immediate confidence as to the likelihood of the correctness of this model. One more atom (Na 12) had to be added out from the center of each hexagon of the Laves–Friauf polyhedron and possibly one additional atom at the center of each such polyhedron (point set 4(*d*), marked *VD* for void in Fig. 1), which appeared to be somewhat crowded.

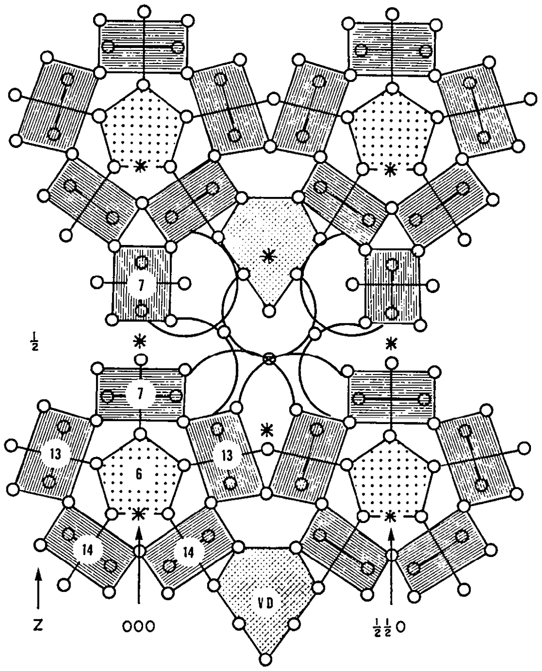

Fig. 1. Packing map of the structure of Na_6Tl, representing the 'most useful plane' [(110) plane] for space group $F\bar{4}3m$. The asterisks indicate the location of the fourfold inversion centers. The polygonal sections marked 7, 13, and 14 represent icosahedra arranged approximately about fivefold axes of symmetry. Comparison of this figure with Fig. 1 in the paper describing Cu_4Cd_3 (Samson 1967*b*) shows that the Na_6Tl structure type represents part of the structural motif of Cu_4Cd_3.

This distribution of atoms, which corresponds to the one given in Table 2, accounts for one formula unit of $Na_{356}Tl_{56}$ or $Na_{352}Tl_{56}$ (if 4(*d*) is empty) per unit cube. This agrees well with the content of about 412 atoms expected on the basis of average atomic volumes discussed in the preceding section.

With the atoms placed according to the 15 different point sets given in Table 2, the structure model was tested and refined by least-squares calculations including the 19 positional parameters, the 15 isotropic temperature factors, and the scale factors in one 35×35 matrix.

The calculations were done with the use of the *CRYM* system on an IBM 360/75 computer. The quantity minimized was $\sum w(F_o^2-S^2F_c^2)^2$, where $1/S$ is the scale factor of F_o and the weighting scheme is that described by Peterson & Levy (1957), modified so as to apply to F^2 rather than to F. All the R values quoted below are defined as $\sum||F_o|-|F_c||/\sum|F_o|$. The atomic scattering factors for Na and Tl were taken from Cromer & Waber (1965) and the anomalous dispersion correction factors from Cromer (1965). These were applied according to the scheme given by Dauben & Templeton (1955).

The first refinement was done using intensity data obtained from an irregular crystal at the Ames Laboratory. The refinement converged rapidly, resulting in an R of 0·16. The center of the Laves–Friauf polyhedron was found to be unoccupied as evidenced by a very high temperature factor for the assumed atom Na (15) (see Table 2).

As the new data became available, the refinement was first continued using all the 615 reflections having net intensities I larger than $\sigma(I)$. Evidence was obtained, again, that the point set 4(*d*) was occupied to only a small extent, or was perhaps empty, and the agreement index R was 0·064. Inclusion of all the 1602 intensity data in the refinement did not result in a significant change of the positional parameters, but in a noticeable improvement of the standard deviations, and a slight increase in some of the temperature factors.

In the final refinement cycles employing all 1602 data, two population parameters p were included, one for Na(8), which had a comparatively high temperature factor, and one for point set 4(*d*) [void (15)]. The temperature factor for (4*d*) was fixed somewhat arbitrarily at $B=5.0$ and excluded from the refinement. In addition, a secondary-extinction parameter g was applied according to equation (3) of the paper by Larson (1967), the matrix now being 37×37. The largest final shift was close to one third of its standard deviation.

The final R value obtained with all data included was 0·137, which is considered reasonable in view of the exceptionally large number of very weak reflections and the scattering from the capillary. The final goodness-of-fit was 1·12, and the extinction parameter refined to $g=(3\cdot53\pm0\cdot15)\times10^{-9}$.

The final positional parameters, the population factors, and the isotropic temperature factors are listed in Table 2 and the structure factors in Table 1. Because of the close coupling with the temperature factors, the population parameters may be of questionable accuracy.

The chemical formula that corresponds to the refined model may be taken as $Na_{352}Tl_{56}$ or $Na_{6.29}Tl$ ($\varrho_{calc}=2\cdot302$ g.cm^{-3}). Because of the possibility of variable composition, especially in possible isostructural compounds (see below), it seems practical to retain the name Na_6Tl for this structure type.

Cursory anisotropic refinement

The relatively large magnitude of the isotropic temperature factors is most likely due to the low melting point of the compound (78 °C; see Introduction), which, in turn is reflected in the softness of the crystals. In order to obtain some idea about the anisotropy of the thermal motions, three additional least-squares calculations were carried out, this time with the use of program *XFLS*.*

The parameters listed in Table 2 were used as a starting point. Full occupancy was assumed of all positions except for 'void 15', which was taken to be occupied 19% of the time by sodium, with B(iso) fixed at 5·0 (as before). The result is shown in Table 3.

The positional parameter X of Na(2) changed from 0·08984 (Table 2) to 0·09126, the parameter Z of Na(3) changed from 0·52856 to 0·52985, and the parameter X of Na(12) from 0·67234 to 0·67521. The changes in the other positional parameters were equal to, or less than three standard deviations.

The R value for the 615 reflections having net intensities I larger than $\sigma(I)$ decreased from 0·064 to 0·050. The overall R value, for 1599 reflections, including 312 data representing zero intensity, is 0·186.

Since the program has no provision for refining the extinction parameter g discussed in the preceding section, the two strongest reflections, 066 & 228, were excluded from the refinement.

It is seen that the atoms Na(5) and Na(12) constituting the Laves–Friauf polyhedron show the most pronounced anisotropy.

Description of the structure

Each of the 56 thallium atoms is surrounded by an icosahedron of 12 sodium atoms. The structure can be described most conveniently in terms of a complex consisting of 14 such icosahedra as shown in Fig. 2. Five icosahedra are arranged approximately about a fivefold axis of symmetry [Fig. 2(*a*)], thus enclosing a pentagonal prism. These icosahedra are the ones that have been marked 7, 13, and 14 on the packing map Fig. 1. Six such fivefold rings interpenetrate one another and share icosahedra so as to form the aggregate shown in Fig. 2(*c*), which consists of 14 icosahedra that enclose six pentagonal prisms of the kind shown at the center of Fig. 2(*a*). The center of each such prism is located at the vertex of an octahedron of T_d symmetry. Fig. 2(*b*) shows two such fivefold rings interpenetrating at right angles. It is now seen that the pentagonal prism at the center of Fig. 2(*a*) is shared between two icosahedra, one above and the other below the plane of the paper. The two icosahedra have one vertex in common at the center of that pentagonal prism, and each icosahedron center is at an extended pole of that prism. Each additional vertex that is shared between two icosahedra represents the center of a pentagonal prism (which has two atoms at its extended poles), as seen in Fig. 2(*c*). Accordingly, 36 more pentagonal prisms are created.

The aggregate shown in Fig. 2(*c*), accordingly, represents 14 icosahedra and 42 pentagonal prisms,

Table 3. *Anisotropic thermal parameters for* Na_6Tl

The expression used was of the form: $-[B'_{11}h^2+B'_{22}k^2+B'_{33}l^2+2B'_{12}hk+2B'_{13}kl+2B'_{23}kl]$. The standard deviations are given in parentheses, and $B'_{ij}=4a_0^2\,B_{ij}$(Å^2).

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na(1)	5·9 (2)	B_{11}	4·1 (4)	0·3 (3)	−1·1 (2)	B_{13}
Na(2)	6·3 (3)	B_{11}	6·7 (5)	0·1 (4)	0·8 (3)	B_{13}
Na(3)	5·8 (3)	B_{11}	6·7 (5)	1·1 (4)	−0·5 (3)	B_{13}
Na(4)	5·4 (2)	B_{11}	5·5 (5)	−0·6 (3)	0·7 (2)	B_{13}
Na(5)	4·8 (2)	B_{11}	8·0 (5)	−0·7 (3)	0·3 (2)	B_{13}
Na(6)	6·7 (5)	4·2 (3)	B_{22}	0	0	−0·1 (5)
Tl(7)	2·96 (5)	4·92 (5)	B_{22}	0	0	−0·19 (7)
Na(8)	7·9 (9)	7·5 (5)	B_{22}	0	0	0·5 (7)
Na(9)	4·5 (4)	B_{11}	B_{11}	−0·8 (3)	B_{12}	B_{12}
Na(10)	4·8 (4)	B_{11}	B_{11}	0·4 (3)	B_{12}	B_{12}
Na(11)	4·4 (3)	B_{11}	B_{11}	0·7 (4)	B_{12}	B_{12}
Na(12)	5·0 (3)	B_{11}	B_{11}	2·2 (4)	B_{12}	B_{12}
Tl(13)	3·56 (2)	B_{11}	B_{11}	0·37 (5)	B_{12}	B_{12}
Tl(14)	3·20 (2)	B_{11}	B_{11}	0·03 (2)	B_{12}	B_{12}

---

* *XFLS* is an IBM-360 version of *ORFLS* (Busing, Martin & Levy, 1962).

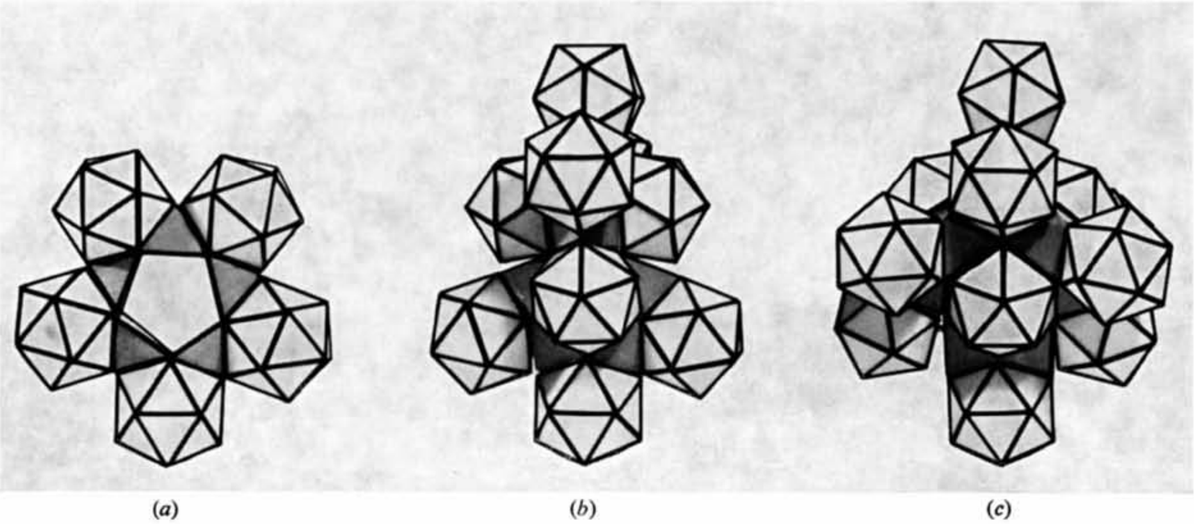

Fig. 2. (*a*) The basic building block of Na_6Tl consisting of an aggregate of five icosahedra arranged approximately about a fivefold axis of symmetry. (*b*) Two such fivefold rings interpenetrating at right angles in such a way that the central pentagonal prism in (*a*) is shared by two icosahedra. (*c*) Six interpenetrating fivefold rings forming a complex of 14 icosahedra and 42 centered pentagonal prisms.

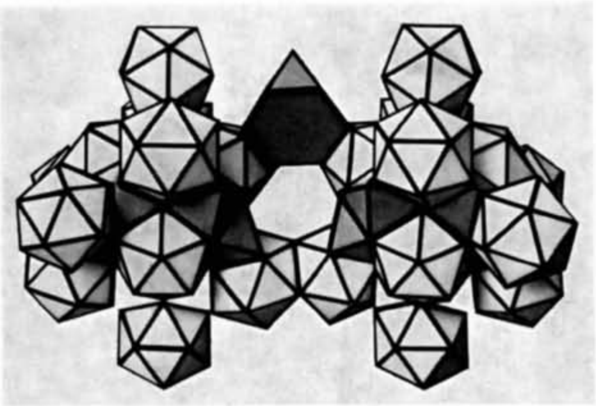

Fig. 3. Two icosahedral complexes of the kind shown in Fig. 2(*c*) sharing one equilateral triangle each with a Laves–Friauf polyhedron (dark), the center of which is a fourfold inversion center. Hence, each Laves–Friauf polyhedron is shared between four such complexes which are tetrahedrally arranged around the $\bar{4}$ center. For the sake of perspicuity one icosahedron has been removed from each 98-atom complex.

each one with two atoms at the extended poles. It is almost identical to one of the four aggregates observed in the structure of Cu_4Cd_3 (Samson, 1967*b*), which, however, contains 1124 atoms per smallest unit cube.

The unit cell of Na_6Tl contains four aggregates of the kind shown in Fig. 2(*c*). These are arranged about the points, 0,0,0, *etc.* [point et 4(*a*)], and share edges and faces in such a way that the average number of atoms per aggregate is 98. Thus, the four aggregates account for 392 atoms per smallest unit cube. With the addition of 16 more atoms [16 Na(12)], each one out from the center of a hexagon of a Laves–Friauf polyhedron, the entire complement of 408 atoms in the unit cell is accounted for.

Fig. 3 shows two icosahedral (98-atom) complexes, each one sharing a triangle with the Laves–Friauf polyhedron (dark) the center of which coincides with a fourfold inversion center. Thus it is seen that each Laves–Friauf polyhedron is shared between four icosahedral complexes that are tetrahedrally arranged around a $\bar{4}$ center. As has already been noted, the center of the Laves–Friauf polyhedron ('void' in Table 2) is probably not occupied.

Other complex cubic A_6B compounds

The crystal-structure studies at this laboratory have revealed, so far, that there exist at least two types of complex cubic A_6B compounds with similar unit-cell contents: the Na_6Tl type containing 408 atoms per structural unit and the Mg_6Pd type (Samson, 1972) containing 396 atoms. Further structural details, including the interatomic distances, which account for similarities as well as the differences between the two types are discussed in the paper following this one (Samson, 1972).

Since the refined structure model does not differ from the original one communicated to the Ames Laboratory, and the shortest Tl–Tl distance observed is 5·631 Å, the general structural features of Na_6Tl discussed by Greiner, *et al.* (1969) are still valid.

We thank Dr Richard Stanford for his valuable help in modifying the Varian 620i computer program to serve our special needs and for having written the IBM programs to process our intensity data. We also thank Mr Benes Trus and Mrs Jean Westphal for their successful effort in adapting the *CRYM* system to our refinement problem and for other valuable aid with computing problems. We express our special appreciation to Professor Jack Smith (Ames Laboratory) for having evidenced paramount and enduring interest in the structure studies of intermetallics conducted in this laboratory, and for the exchange of useful ideas.

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