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The Crystal Structure of α-Li_3AlF_6*

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The crystal structure of the room-temperature modification of Li_3AlF_6 has been determined by three-dimensional X-ray diffraction methods. Crystals are orthorhombic, with unit-cell dimensions $a = 9{\cdot}510$, $b = 8{\cdot}2295$, $c = 4{\cdot}8762$ Å. Each of the ten atoms of the formula occupies a general fourfold site of space group $Pna2_1$. Nearly regular AlF_6 octahedra are linked by Li ions, each of which has six F neighbors at distances in the range 1·87 to 2·42 Å. The Al–F bond lengths vary from 1·786 to 1·830 Å. Although the pseudo face-centered cubic array of AlF_6 octahedra in α-Li_3AlF_6 is similar to that of Na_3AlF_6, its deviations from the ideal cryolite structure are considerable. It is unlikely that Li_3AlF_6 transforms to the ideal cryolite structure at elevated temperature.

Introduction

The structure of the mineral cryolite, Na_3AlF_6, determined by Náray-Szabó & Sasvári (1938), is actually monoclinic; but in an idealized cubic form it is recognized as a structure type for a family of related fluorides. These include K_3AlF_6, K_2NaAlF_6, $(NH_4)_3AlF_6$, and $(NH_4)_3FeF_6$. Steward & Rooksby (1953) studied the structural transitions of these compounds and found that each one becomes cubic at elevated temperature if it is not at room temperature, or else distorts at low temperature if cubic at room temperature. They infer that the non-cubic modifications result from rotation of the AlF_6 (or FeF_6) octahedra out of the most symmetrical orientation as the F atoms are shifted to accommodate alkali cations of various sizes. One exception is K_2NaAlF_6 which remains cubic at all temperatures investigated because both kinds of cations are suitably coordinated in the cubic structure. Winkler (1952, 1954) found that below 470°C K_2LiAlF_6 has a rhombohedral structure which becomes trigonal above this temperature. The fact that these two structures resemble cryolite in the arrangement of octahedra but that the compound never exhibits the cubic form is likely due to the inability of Li to have 12-fold coordination even at elevated temperature.

According to Garton & Wanklyn (1965) Li_3AlF_6 has five polymorphic forms between room temperature and its melting point (783°C). We undertook a single-crystal study of the room temperature form, α-Li_3AlF_6, because we felt that if a relationship to cryolite could be shown, some understanding of these polymorphs could be had in view of the ease with which cryolite transforms by rotation of the AlF_6 groups.

Experimental

Lithium aluminum fluoride was prepared from a stoichiometric mixture of reagent grade LiF and commercial grade AlF_3 which had been purified by distillation. The components were melted together at about 780°C in an evacuated nickel vessel. X-ray powder diffraction indicated the product to be mainly the α phase. A single-crystal specimen of about 0·2 mm in largest dimension was selected for study. Although it was irregular in shape, absorption effects were negligible because of the light atoms of the compound.

Precession and Weissenberg photographs showed the systematic absence of $h0l$ when h is odd and $0kl$ when $k+l$ is odd. These are characteristic for space groups $Pna2_1$ and $Pnam$; the latter was ruled out because a mirror plane perpendicular to the short axis of the crystal would make spatial requirements incompatible with the atomic sizes. The orthorhombic unit cell has dimensions of $a = 9{\cdot}510$ (1), $b = 8{\cdot}2295$ (3), $c = 4{\cdot}8762$ (1) Å. These values were obtained from least-squares adjustment to 35 single-crystal diffractometer 2θ angles, primarily of axial reflections (Cu $K\alpha_1 = 1{\cdot}54051$ Å). There are four formula units in the primitive cell.

Intensity data were obtained from HKl layers with $l = 0$ to 4 by the Weissenberg triple-film technique and Cu $K\alpha$ X-rays. A calibrated film strip was used to evaluate the intensities by visual comparison. About 240 independent reflections were measured and their intensities reduced to structure amplitudes in the usual manner. After the structure was solved, data of higher accuracy appeared desirable, so 617 reflections were measured by 2θ scans with a General Electric single-crystal orienter and a scintillation-counter detector. Data out to $2\theta = 60°$ were collected employing Mo $K\alpha$ radiation. Only these counter-measured data were used for the structure refinement.

The X-ray powder pattern was recorded with a diffractometer and agreed with that reported for α-Li_3AlF_6 by Garton & Wanklyn (1965). It was indexed on the basis of the orthorhombic cell given above, and the intensities calculated from the structure described herein agree with their observed values. Thus, their hexagonal unit cell for the α-modification is erroneous. Probably their indexing of the patterns of the two other forms should be considered only tentative also, espe-

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cially since they require large unit cells and many absences. The cubic phase, for example, shows no reflections with a quadratic form less than 10.

Structure determination

A three-dimensional Patterson function calculated with the Weissenberg intensity data was interpreted to yield the positions of one Al and six F atoms in the general sites of space group $Pna2_1$. An electron density map was then evaluated with the phases calculated from these seven atoms and the observed minus calculated amplitudes. This partial difference Fourier synthesis yielded peaks for the location of the three independent Li atoms. A refinement of these positions and individual isotropic temperature factors by the method of least squares resulted in a structure with a conventional R value of 0·13. For calculation of structure factors the scattering curves for Li^+, Al^{3+}, and F^- were taken from *International Tables for X-ray Crystallography* (1962).

The counter-measured data were then collected and refinement was resumed with the addition of anisotropic temperature factors. Shifts in positions from the earlier structure averaged about 0·3, 0·1, and 0·05 Å for Li, F, and Al atoms, respectively; and the discrepancy factor dropped sharply. Values of the refined parameters and their standard errors are given in Table 1. The nineteen strongest reflections were omitted from the final refinement cycles because they were observed systematically to be weaker than the calculated values, probably because of secondary extinction. The discrepancy index, $R = \Sigma\,||F_o|-|F_c||/\,\Sigma\,|F_o|$, for the other 598 reflections was 0·017.

The full-matrix least-squares program of Busing, Martin & Levy (1962) was used for the refinement. The weight, w, of each observation was taken equal to the reciprocal of its variance which was calculated from the counting statistics plus 3% of the intensity as an estimate of the other errors in the measurements. At the end of the refinement the standard deviation of an observation of unit weight, $[\Sigma\, w(F_o^2-F_c^2)/(n_o-n_v)]^{\frac{1}{2}}$, was 1·0. In this expression n_o and n_v are numbers of observations and variables, respectively.

In Table 2 are listed the values of the observed and calculated structure factors and the phase angles.

Results and discussion

The structure of α-Li_3AlF_6 is represented in Fig. 1 by a stereoscopic pair of drawings including a little more than the contents of one unit cell. For clarity of representation atoms are shown as small circles. The F atoms around each Al atom are connected by lines to make an octahedron; the Li atoms are between the

Table 1. *Final structure parameters and standard errors* (× 10^5) *for* α-Li_3AlF_6

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$\beta_{11}{}^*(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Al	12779 (4)	24031 (3)	0†	153 (3)	145 (4)	398 (13)	−9 (2)	0 (4)	0 (8)
F(1)	22373 (7)	6821 (8)	14055 (26)	271 (7)	276 (9)	804 (34)	72 (6)	37 (14)	88 (17)
F(2)	2326 (8)	24326 (7)	30699 (23)	258 (7)	377 (9)	743 (40)	−31 (6)	122 (15)	−40 (13)
F(3)	23609 (7)	23421 (8)	69815 (22)	261 (7)	389 (10)	632 (41)	−50 (6)	122 (15)	−34 (15)
F(4)	2888 (7)	40216 (8)	85078 (24)	304 (7)	319 (8)	936 (33)	110 (7)	26 (16)	97 (15)
F(5)	24358 (7)	38174 (8)	17257 (25)	264 (6)	313 (9)	877 (35)	−84 (6)	−32 (14)	−52 (16)
F(6)	1361 (6)	9168 (8)	83164 (24)	269 (7)	314 (8)	848 (35)	−104 (6)	−1 (14)	−82 (14)
Li(1)	37529 (21)	34902 (28)	50727 (79)	292 (20)	663 (30)	1776 (90)	−15 (20)	258 (38)	−60 (70)
Li(2)	10546 (22)	45729 (27)	49687 (93)	311 (20)	547 (28)	1372 (88)	22 (20)	−28 (58)	218 (61)
Li(3)	35387 (22)	54574 (26)	235 (92)	386 (21)	462 (27)	957 (81)	−96 (19)	23 (58)	−8 (59)

* Coefficients in the temperature factor expression: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

† Arbitrary value to establish origin on 2_1 axis.

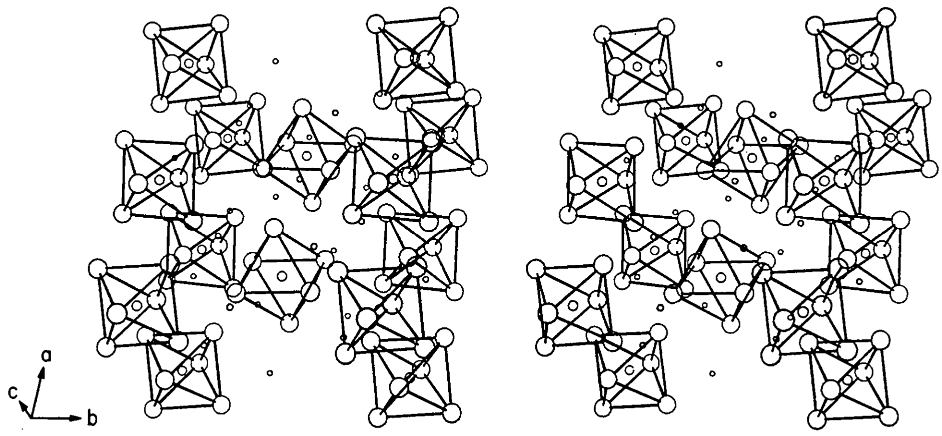

Fig. 1. Stereoscopic pair of drawings of the structure of α-Li_3AlF_6.

octahedra. The lattice on which the octahedra are arrayed is very similar to the one in Na_3AlF_6, a fact that will be examined in detail later.

Interatomic distances and their standard errors are listed in Table 3. These include all the cation–anion contacts as well as the F–F distances within one octahedron. The next nearest Li–F distance is greater than 3·0 Å. It is noteworthy that the five shortest F–F distances are within edges of the AlF_6 octahedron which are shared with Li atoms: one with Li(1), two with Li(2), and two with Li(3). Expressed differently, the F–Al–F angles subtended by the shared edges average 87·75° compared with 91·60° for the unshared edges. This is a good example of the effect of repulsion of the cations sharing an edge, as stated in Pauling's (1960) fourth rule for the stability of complex ionic crystals.

In Fig. 2 more details of coordination and thermal motion are shown. Each cation and its surrounding

Table 2. *Observed and calculated structure factors* (× 10) *and phase angles* (*millicycles*)
Reflections omitted from the refinement are denoted by X after the first Miller index.

H	OBS	CAL	ANG
H 0 0			
2	34	33	0
4X	678	863	0
6	45	43	0
8X	641	714	0
10	109	111	0
12	114	114	0
H 1 0			
1	112	110	0
2X	603	681	0
3	151	144	0
4	79	79	0
5	189	195	0
6	183	178	0
7	50	49	0
8	104	103	0
9	112	114	0
10	425	445	0
11	39	33	0
12	23	9	0
13	78	80	0
H 2 0			
0X	427	445	0
1	52	51	0
2	20	17	0
3	59	59	0
4	134	131	0
5	133	131	0
6	13	14	0
7	60	61	0
8	273	278	0
9	67	67	0
10	82	85	0
11	42	40	0
12	106	105	0
13	56	58	0
H 3 0			
1	97	91	0
2	160	151	0
3	26	27	0
4	25	26	0
5	127	128	0
6	380	396	0
7	79	80	0
8	21	21	0
9	54	54	0
10	74	73	0
11	12	8	0
12	38	37	0
H 4 0			
0	170	169	0
1	62	62	0
2	60	60	0
3	161	163	0
4	401	403	0
5	23	25	0
6	11	13	0
7	29	29	0
8	135	130	0
9	44	44	0
10	15	16	0
11	10	0	0
12	149	146	0
H 5 0			
1	100	99	0
2X	516	569	0
3	48	46	0
4	29	27	0
5	60	61	0
6	71	67	0
7	3	11	0
8	20	18	0
9	21	23	0
10	345	348	0
11	110	111	0
12	27	28	0
H 6 0			
0X	789	935	0
1	411	417	0
2	101	101	0
3	165	166	0
4	282	288	0
5	148	149	0
6	61	62	0
7	109	108	0
8	312	315	0
9	211	211	0
10	39	39	0
11	17	16	0
H 7 0			
1	140	136	0
2	254	261	0
3	74	73	0
4	89	90	0
5	119	120	0
6	52	52	0
7	8	2	0
8	122	122	0
9	140	138	0
10	288	286	0
H 8 0			
0	315	320	0
1	144	145	0
2	30	24	0
3	28	27	0
4	1	6	0
5	33	33	0
6	11	6	0
7	113	110	0
8	224	224	0
9	68	68	0
H 9 0			
1	54	55	0
2	146	145	0
3	11	12	0
4	24	22	0
5	82	79	0
6	172	171	0
7	91	91	0
8	8	3	0
H 10 0			
0	151	153	0
1	2	3	0
2	102	100	0
3	124	126	0
4	192	191	0
5	102	105	0
6	34	36	0
H 11 0			
1	81	83	0
2	121	121	0
3	79	80	0
4	25	28	0
H 0 1			
2X	434	426	-248
4	146	146	-20
6	103	104	-238
8	111	111	49
10	277	284	247
12	53	50	-95
H 1 1			
0X	474	459	246
1	85	81	-242
2	15	15	183
3	82	81	6
4	151	148	-237
5	34	34	-241
6	29	28	-224
7	125	127	125
8	216	220	238
9	77	75	-149
10	31	32	-227
11	92	92	-142
12	114	115	-230
13	67	64	-60
H 2 1			
1	40	39	168
2X	372	369	-237
3	51	50	-88
4	324	328	14
5	40	41	245
6X	490	521	240
7	86	86	-71
8	273	278	-15
9	85	85	162
10	85	86	-220
11	63	63	81
12	165	161	24
13	56	55	82
H 3 1			
0	251	265	215
1	263	261	-35
2X	825	1165	5
3	291	297	-87
4X	681	833	249
5	234	235	-162
6X	471	510	-11
7	129	130	-8
8	124	122	191
9	47	48	98
10	123	123	11
11	59	59	-41
12	143	144	-191
H 4 1			
1	38	37	61
2	143	143	-178
3	140	141	20
4	271	274	48
5	87	89	-183
6	330	338	203
7	175	175	-100
8	255	255	12
9	103	102	-201
10	61	60	-66
11	92	91	46
12	177	173	44
H 5 1			
0	206	207	250
1	69	67	179
2	221	218	23
3	96	94	242
4	248	252	-230
5	35	33	-154
6	142	144	-32
7	41	39	-147
8	154	152	192
9	66	67	-206
10	81	78	-6
11	18	18	113
H 6 1			
1	110	108	-219
2	243	244	246
3	78	80	-227
4	54	55	-12
5	76	76	147
6	91	92	-232
7	17	15	22
8	58	56	78
9	92	93	-178
10	170	170	240
11	51	52	-242
H 7 1			
0	371	379	222
1	137	136	-156
2	74	75	106
3	52	52	-89
4	194	197	-213
5	56	56	14
6	59	58	105
7	73	72	-245
8	202	204	245
9	30	34	-200
10	41	43	-106
H 8 1			
1	66	62	-209
2	194	190	245
3	107	105	222
4	90	87	-7
5	58	60	-174
6	226	226	-242
7	102	102	244
8	108	109	-61
9	73	72	109
H 9 1			
0	110	111	23
1	161	157	-32
2	220	218	43
3	207	204	-86
4	208	211	185
5	178	176	-172
6	115	113	21
7	129	128	3
8	67	68	-167
H 10 1			
1	49	49	-135
2	98	97	-184
3	98	98	103
4	90	90	93
5	105	107	-221
6	166	163	171
H 11 1			
0	83	84	-162
1	73	73	98
2	94	95	58
3	107	106	-159
H 0 2			
0	285	300	4
2X	981	1173	249
4X	862	1016	-2
6X	477	501	-227
8	95	93	94
10	106	107	-218
12	203	202	-35
H 1 2			
1	54	54	-148
2	209	203	-37
3	146	148	114
4	286	287	211
5	69	70	-140
6	427	443	20
7	132	133	-201
8	243	244	248
9	55	54	-44
10	34	33	-228
11	107	106	154
12	158	153	209
H 2 2			
0	23	25	179
1	62	63	68
2	38	38	113
3	100	98	-94
4	397	409	1
5	33	34	116
6	65	66	-30
7	88	89	-225
8	121	120	36
9	50	48	-96
10	30	21	-215
11	82	80	-124
12	149	149	-33
H 3 2			
1	67	67	-0
2	231	232	5
3	81	81	-59
4	168	164	-236
5	104	103	59
6	231	228	-4
7	32	32	135
8	142	143	215
9	59	60	-76
10	136	134	9
11	25	25	-63
12	78	79	-212
H 4 2			
0	248	251	29
1	124	125	225
2	182	174	-240
3	85	84	79
4	288	288	-13
5	83	83	176
6	105	105	214
7	34	34	91
8	173	175	-7
9	22	24	7
10	51	49	-185
11	63	62	-90
H 5 2			
1	71	71	-99
2	317	321	6
3	33	34	38
4	153	155	209
5	38	39	8
6	366	381	-6
7	103	102	64
8	154	153	-245
9	45	47	158
10	76	77	33
11	47	47	223
H 6 2			
0	134	131	126
1	204	203	-206
2	427	443	227
3	253	258	-147
4	398	411	20
5	229	230	-67
6	217	216	-246
7	142	141	-210
8	43	40	-37
9	26	28	232
10	47	44	199
H 7 2			
1	21	18	187
2	110	109	-70
3	117	117	143
4	123	122	189
5	95	95	-69
6	253	255	59
7	125	126	-170
8	140	139	230
9	57	56	-146
H 8 2			
0	38	38	-229
1	55	55	134
2	80	77	-229
3	110	112	-20
4	252	253	10
5	108	108	-60
6	81	80	-180
7	56	58	15
8	53	51	87
H 9 2			
1	38	35	-35
2	148	147	9
3	71	69	-66
4	43	42	-231
5	77	79	78
6	132	136	-18
7	34	35	147
H 10 2			
0	185	186	84
1	102	99	-136
2	45	45	194
3	73	73	152
4	166	166	-65
5	84	83	121
H 11 2			
1	52	54	-25
H 0 3			
2	163	165	-243
4	135	129	-30
6	340	345	-247
8	134	133	19
10	74	74	-234
12	81	80	-73
H 1 3			
0	156	158	-246
1	116	117	-54
2	225	221	-6
3	94	92	138
4	262	263	240
5	107	109	-113
6	107	107	28
7	73	72	-238
8	135	133	-231
9	63	41	-173
10	42	42	-139
11	21	21	121
12	120	122	226
H 2 3			
1	54	55	21
2X	512	507	246
3	34	35	-200
4	21	19	49
5	99	98	121
6	51	50	-148
7	50	50	-136
8	52	53	165
9	59	59	171
10	339	340	242
11	49	49	-130
H 3 3			
0X	1022	1168	249
1	244	246	-235
2	64	64	74
3	82	81	-233
4	265	266	-247
5	64	65	-209
6	53	56	39
7	71	73	-207
8	403	416	-244
9	132	130	-227
10	80	80	-153
11	12	14	-139
H 4 3			
1	100	99	168
2	294	293	250
3	63	62	-225
4	65	66	171
5	134	133	190
6	65	64	-220
7	31	31	-121
8	102	100	192
9	95	93	210
10	293	295	-247
11	57	56	188
H 5 3			
0	321	322	-220
1	53	54	211
2	166	165	-9
3	37	38	171
4	80	78	172
5	80	78	-188
6	95	95	-26
7	49	48	-114
8	227	225	-232
9	22	19	40
10	74	75	-207
H 6 3			
1	69	69	197
2	136	134	245
3	45	46	-76
4	73	73	-46
5	94	93	238
6	209	209	-247
7	83	82	176
8	78	80	5
9	45	46	-178
H 7 3			
0	163	158	212
1	68	70	71
2	95	96	-107
3	126	127	174
4	278	280	-234
5	78	77	164
6	43	44	-21
7	23	19	24
8	89	91	-244
H 8 3			
1	86	86	-208
2	223	222	237
3	80	81	246
4	21	23	-239
5	46	45	185
6	61	63	-163
7	29	33	188
H 9 3			
0	292	292	241
1	203	204	-241
2	88	90	231
3	66	64	-232
4	53	54	221
5	82	80	-217
6	68	68	221
H 10 3			
1	106	109	231
2	134	131	-237
3	47	50	-229
H 0 4			
0	95	96	43
2X	552	574	-243
4	501	504	4
6	323	324	240
8	168	167	-36
10	119	118	-218
H 1 4			
1	59	58	139
2	205	200	15
3	52	52	186
4	158	158	-218
5	51	50	-69
6	252	251	-30
7	104	104	86
8	186	183	241
9	82	85	-55
10	79	80	50
H 2 4			
0	375	374	-8
1	52	52	-198
2	138	136	-200
3	69	71	-147
4	53	51	99
5	51	49	188
6	74	74	248
7	57	59	-114
8	197	193	-25
9	78	80	104
10	41	40	-135
H 3 4			
1	82	80	33
2	262	260	-0
3	42	42	-25
4	13	9	168
5	25	26	-65
6	14	14	171
7	9	4	163
8	26	28	-69
9	61	63	41
10	245	243	-6
H 4 4			
0	400	401	0
1	107	109	-26
2	28	28	-110
3	66	65	-43
4	54	52	-10
5	29	30	-37
6	28	28	-140
7	88	88	-54
8	208	206	0
9	17	20	212
H 5 4			
1	19	20	-109
2	245	241	9
3	83	82	8
4	91	90	227
5	36	37	203
6	255	250	-10
7	23	25	-59
8	120	119	179
9	80	82	-112
H 6 4			
0	69	68	200
1	120	121	-248
2	278	278	-231
3	159	158	173
4	246	244	-34
5	146	144	93
6	172	168	246
7	102	103	-225
8	89	87	8
H 7 4			
1	46	47	144
2	107	105	38
3	67	67	-209
4	109	108	-173
5	67	68	-3
6	147	146	-52
7	96	98	119
H 8 4			
0	171	169	-8
1	77	78	-64
2	140	139	-202
3	80	82	77
4	72	76	45
5	19	22	134
H 9 4			
1	76	76	35
2	149	148	-3
3	45	45	-61
H 0 5			
2	127	127	-234
4	116	116	9
6	227	225	245
8	126	128	-32
H 1 5			
0	37	36	209
1	70	70	-162
2	139	139	3
3	109	107	247
4	247	245	-247
5	47	46	-148
6	93	93	-44
7	40	41	91
8	86	86	226
9	18	18	189
H 2 5			
1	41	44	133
2	207	205	-249
3	62	64	-202
4	87	88	-78
5	18	15	-94
6	265	265	-246
7	67	66	-120
8	88	86	-19
H 3 5			
0	32	33	23
1	62	61	22
2	281	278	-14
3	92	91	141
4	384	388	-241
5	96	97	207
6	150	150	26
7	51	53	59
8	31	32	-230
H 4 5			
1	26	24	207
2	95	95	203
3	91	91	-171
4	78	77	-51
5	38	38	118
6	213	213	-218
7	67	68	17
H 5 5			
0	45	43	-196
1	42	42	-244
2	51	50	-148
3	31	30	-40
4	265	265	-242
5	46	47	222
6	48	51	-244
7	75	70	156
H 6 5			
1	13	16	-206
2	97	100	-240
3	55	56	162
4	67	70	13
5	80	84	-205
H 7 5			
0	141	138	-189
1	80	80	-9
2	107	104	35
3	82	82	-134
4	172	170	222
H 0 6			
0	495	502	2
2	51	52	-200
4	36	36	19
6	62	58	-210
H 1 6			
1	51	52	-144
2	194	194	-5
3	20	19	95
4	32	28	-175
5	71	70	-156
6	31	30	22
H 2 6			
0	117	120	42
1	55	56	174
2	158	159	242
3	18	26	87
4	128	128	-32
5	76	75	128
6	100	97	-243
H 3 6			
1	32	31	-58
2	96	98	0
3	28	30	164
4	89	90	216
5	33	35	-1
H 4 6			
0	62	64	-67
1	71	72	246
2	111	112	242
3	70	71	-156
4	203	202	10
H 5 6			
1	40	40	152
2	193	190	-10
H 6 6			
0	276	275	-8

Table 3. *Interatomic distances and standard errors*

	Distance	$(10^3\,\sigma)$		Distance	$(10^3\,\sigma)$
Al–F(4)	1·786 Å	(1)	Li(1)–F(2)	1·874 Å	(3)
F(2)	1·797	(2)	F(3)	1·874	(3)
F(3)	1·797	(1)	F(5)	2·075	(4)
F(5)	1·810	(1)	F(6)	2·114	(4)
F(1)	1·819	(1)	F(1)	2·136	(3)
F(6)	1·830	(1)	F(6)	2·416	(3)
Li(2)–F(4)	1·865	(3)	Li(3)–F(5)	1·900	(3)
F(4)	1·927	(5)	F(1)	1·921	(5)
F(1)	1·991	(3)	F(3)	2·012	(3)
F(2)	2·138	(3)	F(6)	2·069	(3)
F(5)	2·148	(4)	F(6)	2·076	(4)
F(3)	2·424	(3)	F(2)	2·217	(3)
F(1)–F(2)	2·524	(1)	F(2)–F(6)	2·634	(2)
F(3)	2·556	(2)	F(3)–F(4)	2·519	(1)
F(5)	2·592	(1)	F(5)	2·614	(2)
F(6)	2·510	(1)	F(6)	2·505	(1)
F(2)–F(4)	2·581	(2)	F(4)–F(5)	2·581	(1)
F(5)	2·473	(1)	F(6)	2·561	(1)

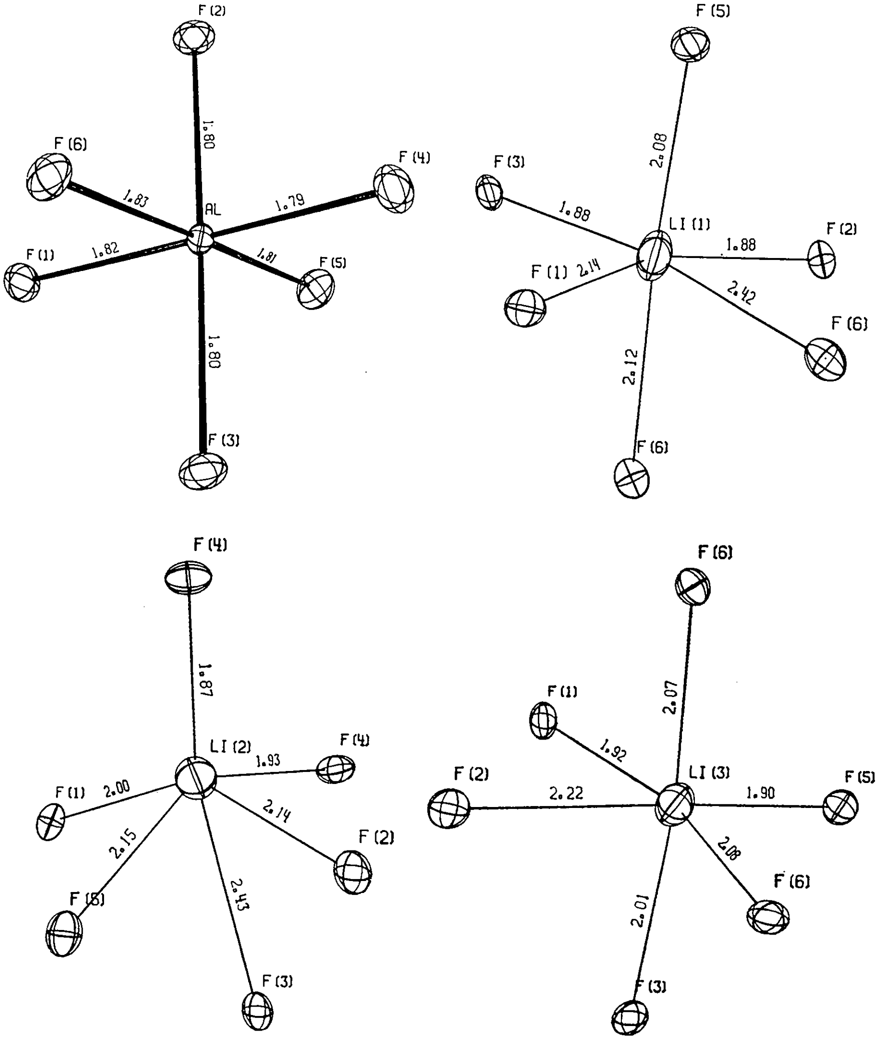

Fig. 2. Coordination polyhedra for each cation. Atoms are represented by thermal ellipsoids.

octahedron of F atoms is illustrated by means of the 50% probability ellipsoids of thermal motion derived from the temperature factors (Johnson, 1965). From the shapes and orientations of these ellipsoids the greater influence on the thermal motion of the F atoms by the Al–F bonds than by the Li–F bonds is apparent. Both kinds of bond are principally ionic in character, but the Al–F electrostatic bond strength is greater by at least a factor of three. Thus the F atoms vibrate more perpendicular to the Al–F lines than along them, while the presence of the Li atoms results in no apparent constraints on the thermal motion. Also it appears that the nearly regular AlF_6 octahedra are achieved at the expense of regularity around the Li atoms, which have six neighbors but with a wide range of distances.

It is important to compare the structure of α-Li_3AlF_6 with that of cryolite because the latter is a well known structure type. Steward & Rooksby (1953) have examined the family of compounds related to cryolite and have concluded that while they all have the basic feature of a three-dimensional framework of AlF_6 octahedra linked by alkali ions, some members have the octahedra rotated out of the most symmetrical orientation. These workers also observed that at elevated temperatures the misorientation and distortions, wherever present, were removed and the cubic symmetry of the idealized cryolite structure achieved.

A comparison of the structures of cryolite and α-Li_3AlF_6 is shown in Fig. 3. The pseudo-cubic cells shown are chosen in such a way as to emphasize the relationship to the idealized cubic cryolite structure rather than to show the actual crystal symmetries which are monoclinic and orthorhombic, respectively. The idealized structure is visualized by rotating the octahedron* in the cryolite structure so that its four-fold axes point along the cube edges. Then the Na atoms on the edges are in octahedral coordination, and the Na atoms within the cell (larger circles for ease of distinction) have 12 F neighbors, three from each of the four AlF_6 octahedra around it. Indeed, this is pre-

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* The octahedra on the left and right faces of the cube are oriented the same, but those centered in the other faces are in a symmetry related orientation. This difference disappears in the idealized structure.

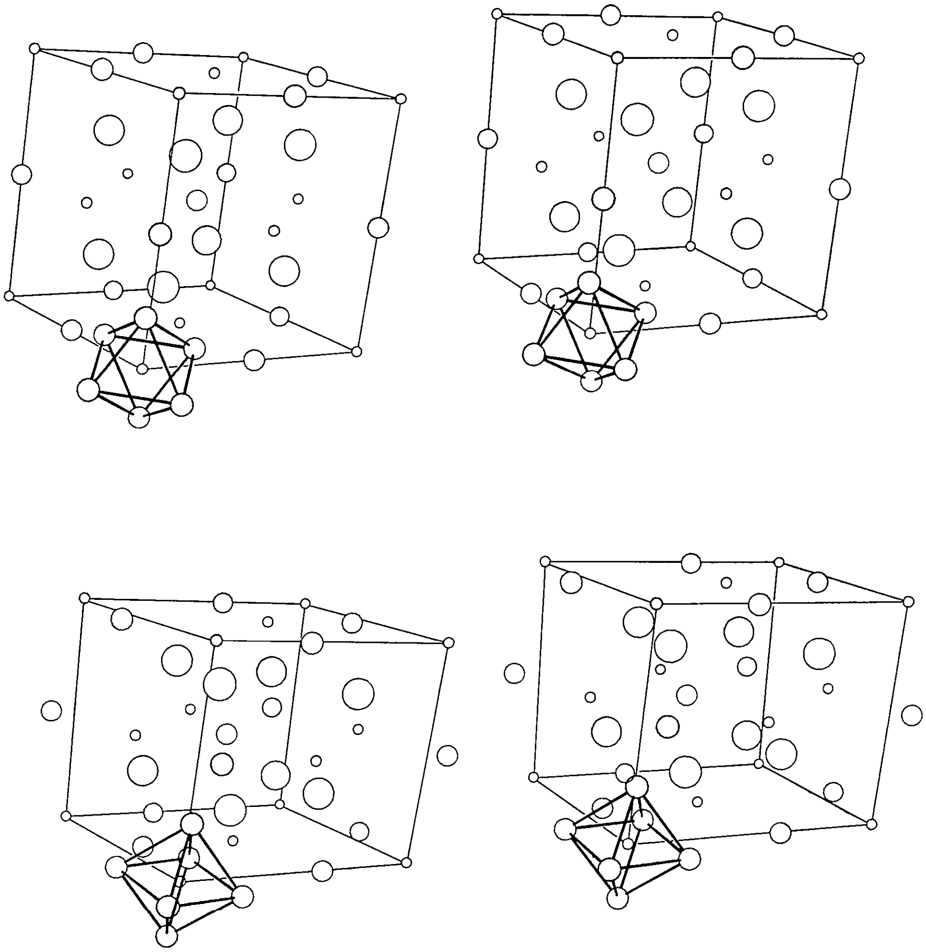

Fig. 3. Comparison of the structures of cryolite (upper) and α-Li_3AlF_6. The smallest circles represent Al atoms. Only one octahedron of F atoms is shown, but each Al atom has an octahedron associated with it. Medium and large circles distinguish cations, Na or Li in the respective structures, which are identical except for symmetry.

sumed to be the structure of Na_3AlF_6 when it becomes cubic at 540°C. In the structure of K_2NaAlF_6, which is cubic at all temperatures studied, K atoms occupy the sites within the cube and Na atoms the sites on the edges.

The deviations from the ideal cryolite structure are greater in α-Li_3AlF_6 than in Na_3AlF_6, but the similarity can still be recognized by reference to Fig. 3. The octahedra are in a pseudo face-centered cubic array, but the Li atoms are displaced from the center of the edges and the center of the cell. The 'cube' of eight Li atoms within the cell is also quite distorted.

It is unlikely that Li_3AlF_6 exists at any temperature in the idealized cryolite structure in which two thirds of the Li atoms would have 12-fold coordination; but this would not preclude there being a cubic structure of this type which had these Li atoms in a disordered arrangement within the space surrounded by 12 F atoms. The cubic cell assigned by Garton & Wanklyn (1965) to γ-Li_3AlF_6 does not have the proper dimensions indicative of a cryolite structure; in fact, the assignment of cubic symmetry to this phase is questionable as described earlier. On the other hand, δ- or ε-Li_3AlF_6 may be cubic; data are not available for their powder patterns.

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The Crystal Structure of $Na_7Zr_6F_{31}$*

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The structure of $Na_7Zr_6F_{31}$ was determined by single-crystal X-ray and neutron diffraction methods. Zirconium atomic positions were deduced from an X-ray Patterson map, and the remaining atomic sites from electron-density maps. Refinement including anisotropic thermal parameters was carried out by the method of least squares. The neutron scattering amplitude of Zr was determined to be $0{\cdot}69 \pm 0{\cdot}01 \times 10^{-12}$ cm. The rhombohedral unit cell, with $a = 8{\cdot}5689$ Å, $\alpha = 107°21'$, contains one formula weight of $Na_7Zr_6F_{31}$. Six Na atoms, six Zr atoms, and five sets of six F atoms occupy general sixfold positions of $R\bar{3}$, while one Na atom is in a onefold special position and one F atom is statistically distributed over a twofold site. Each Zr atom is bonded to eight F atoms arranged as a square antiprism. Six antiprisms share corners to enclose a cuboctahedral cavity which is occupied by one disordered F atom. This structural feature accounts for the unusual stoichiometry of the compound. The Na atoms are located outside the triangular faces of the cuboctahedron. One edge of each antiprism is shared with an antiprism of a different octahedral group of antiprisms, bridging all groups together.

Introduction

The study of this crystal structure was undertaken primarily because of the curious stoichiometry of the compound. There are a large number of compounds which have this formula type and which, from their X-ray powder patterns, appear to be isostructural. In fact, although the stoichiometry was checked by chemical analysis in some instances, the formula has been assigned to many of these compounds only on the basis of similarity of their powder patterns to those of the well-established 7:6 compounds. Six of these double fluorides were reported by Zachariasen (1948) to have 1:1 composition. Subsequent phase diagram studies by Barton, Friedman, Grimes, Insley, Moore & Thoma (1958) and Barton, Grimes, Insley, Moore & Thoma (1958) showed that they actually have 7:6 ratios, and

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