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The Crystal Structure of $LiUF_5$*

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The compound $LiUF_5$ crystallizes in space group $I4_1/a$ with unit cell parameters $a_0 = 14{\cdot}884$, $c_0 = 6{\cdot}547$ Å. The X-ray density is 6·23 g.cm^{-3} and $Z = 16$. The U^{4+}, Li^+, and $5F^-$ ions occur in positions 16(*f*). Twenty-one positional parameters, six anisotropic uranium temperature factors, and six isotropic temperature factors were determined from 739 independent reflections measured by the 2θ-scan technique with a scintillometer. The parameters were refined by least squares to an R value of 0·072. Absorption corrections were made for an oblate spheroid with a short 55·8μ axis, [$\bar{1}$10], and a 74·4μ diameter for the circular section containing [110] and [001]. The absorption factor μR was 4·16 in the direction of maximum absorption.

The U^{4+} ion has $9F^-$ nearest neighbors with bond distances of 2·26 to 2·59 Å. The F^- ions are at the corners of a 14-faced polyhedron which has the form of a triangular prism with pyramids on each of the three prism faces. The Li^+ ion has $6F^-$ nearest neighbors with bond distances of 1·84 to 2·31 Å. These F^- ions are at the corners of an irregular octahedron.

Introduction

The intermediate compound $LiUF_5$, which was originally described as $Li_7U_6F_{31}$ in the molten salt system LiF-UF_4 (Harris, 1958; Barton, Friedman, Grimes, Insley, Moore & Thoma, 1958; Harris, White & Thoma, 1959; Weaver, Thoma, Insley & Friedman, 1960), melts incongruently and a pure single-phase solid has never been obtained from melts having the composition $LiUF_5$ or $Li_7U_6F_{31}$ (Thoma, 1965). The latter composition was inferred from the fact that sodium and potassium form congruently melting $Na_7U_6F_{31}$ and $K_7U_6F_{31}$ in the systems NaF–UF_4 and KF–UF_4 respectively (Barton *et al.*, 1958; Thoma, Insley, Landau, Friedman & Grimes, 1958) and because the LiF–UF_4 phase was found to be uniaxial negative as were the $7AF\,.\,6MF_4$ phases. The stoichiometry of $Na_7U_6F_{31}$ and $K_7U_6F_{31}$ can be demonstrated easily by equilibrating mixtures of the end members at these compositions. Several other compounds of alkali fluorides and tetravalent metal fluorides have this formula (Thoma, 1962). Their X-ray powder patterns indicate that they all may be isomorphous and that all are rhombohedral. The structure of one of them, $Na_7Zr_6F_{31}$, has been determined by Burns, Ellison & Levy (1966).

The stoichiometry of $Li_7U_6F_{31}$ was questioned for two reasons: (1) the density calculated from the unit-cell parameters and two formula weights per cell (Harris, White & Thoma, 1959) was much lower than the density calculated from the indices of refraction and the measured density (4·73 *vs* 5·8 g.cm^{-3}), and (2) the crystal system and space group (tetragonal, $I4_1/a$) were different from those of the other 7:6 compounds. The value of 5·8 g.cm^{-3} was obtained from pycnometric density measurements on impure crystals. The optical density was estimated from the formula $(n-1)/d = K$ where $K = (k_1P_1)/100 + (k_2P_2)/100 + etc$, n is the average index of refraction, k_i and P_i are respectively the specific refractive energies and weight percentages of the components of the compound, and d is the density (Larsen & Berman, 1934). Both of these densities are estimates but were assumed to give at least the lower limit for the true density of $LiUF_5$. The P_i for the calculation were for $Li_7U_6F_{31}$. The refractive indices are: $n_0 = 1{\cdot}554$ and $n_E = 1{\cdot}550 \pm 0{\cdot}002$.

Experimental

Crystals of $LiUF_5$ were grown in a molten salt of the composition $Na_{0{\cdot}05}Li_{0{\cdot}43}U_{0{\cdot}26}F_{1{\cdot}6}$ because $LiUF_5$ is easily crystallized as the primary phase at this composition (Thoma *et al.*, 1958). The solidified ingot consisted of acicular crystals (50 to 75μ in diameter by several millimeters long) of $LiUF_5$ and a cryptocrystalline matrix. Crystals were separated from the matrix and ground to approximately spherical shape. An oblate spheroid 55·8μ by 74·4μ in diameter was mounted along [110] on a General Electric single-crystal orienter equipped with a scintillation-counter detector. All of the independent reflections hkl out to $2\theta = 148{\cdot}1°$ were measured with Cu $K\alpha$ radiation by the 2θ-scan technique.

The parameters for the unit cell were refined by least-squares fitting of eighteen high angle Cu $K\alpha_1$ (1·5405 Å) reflections to obtain $a_0 = 14{\cdot}884 \pm 0{\cdot}002$, $c_0 = 6{\cdot}547 \pm 0{\cdot}001$ Å. The calculated density is 6·23 g.cm^{-3} with $Z = 16$.

The 739 reflection data were corrected for Lorentz-polarization factors and for absorption and were reduced to structure factors, $|F_o|$. A computer program

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written by Johnson (1965*a*) enables one to make absorption corrections for triaxial ellipsoids of known orientation. In this case the short axis was [$\bar{1}$10] and the two longer equidimensional axes were [110] and [001].

Structure determination

Patterson projections (*hk*0) and (0*kl*) gave the position of the U^{4+} ion at general position 16(*f*) with the origin at the center of symmetry: approximately $x={}^1/_{16}$, $y={}^1/_{16}$, $z={}^1/_4$, and four of the five F^- ions were placed by the heavy atom technique. The position of the fifth F^- ion was determined by a three-dimensional difference synthesis. The Li^+ ion position was determined by difference synthesis and inferences from three-dimensional stereoscopic views of the structure (Johnson, 1965*b*).

The imaginary component of anomalous dispersion of uranium for Cu *Kα* X-rays is large (*International Tables for X-ray Crystallography*, 1962), and its contribution was included in the structure factor calculations. The structure factor is given by

$$F_{hkl}=\sum_N (f_n+\Delta f'+i\Delta f'')_n (\cos\varphi_n+i\sin\varphi_n)$$

where f_n, $\Delta f'$, and $\Delta f''$ are the normal part, the real and imaginary anomalous parts of the scattering factor respectively; $\varphi=2\pi(hx_n+ky_n+lz_n)$ and the sum is taken over all *n* atoms of the unit cell. For computation, $F_c=A+iB_A$ where $A=\sum\limits_N (f_0+\Delta f')_n \cos\varphi_n$ and $B_A=\sum\limits_N \Delta f \;\cos\varphi_n$ for the centrosymmetric case. The values of $\Delta f'=-4$ and $\Delta f''=16$ electrons were used for the anomalous dispersion of uranium (*International Tables*, 1962; Roof, 1961). The normal atomic scattering factors for F^- and Li^+ were taken from the *International Tables* (1962) and for U^{4+} from Cromer & Waber (1965).

The atomic positions, anisotropic temperature factors for uranium and isotropic temperature factors for lithium and fluorine were adjusted by the method of least squares with the use of a CDC 1604 computer and the Busing, Martin & Levy (1962) program. The quantity $\Sigma w(F_o-F_c)^2$ was minimized and the summation was taken over all of the independent reflections. The refinement was based on $|F_o|$ and the corresponding weighting factor was the reciprocal of $\sigma(F_o)$ where $\sigma(F_o)=\frac{1}{2}\sigma(F_o^2)/F_o$. The empirical equation

Table 1. *Atomic parameters for* $LiUF_5$

Atom	$x(\pm10^4\sigma)$	$y(\pm10^4\sigma)$	$z(\pm10^3\sigma)$	$B_{11}(\pm10^4\sigma)$	$B_{22}(\pm10^5\sigma)$	$B_{33}(\pm10^4\sigma)$	$B_{12}(\pm10^5\sigma)$	$B_{13}(\pm10^5\sigma)$	$B_{23}(\pm10^5\sigma)$
U	0·06176(0·4)	0·05649(0·4)	0·2462(0·1)	0·00026(0·3)	0·00015(3)	0·0027(2)	–0·00004(2)	–0·00017(6)	–0·00006(5)
F(1)	0·0361(9)	0·0523(9)	0·873(3)	0·0017(2)					
F(2)	0·2098(9)	0·1754(9)	0·760(3)	0·0018(2)	Isotropic temperature factors				
F(3)	0·1085(9)	0·1831(9)	0·075(2)	0·0013(2)	$B_{22}=B_{11}$				
F(4)	0·2048(10)	0·0918(10)	0·358(3)	0·0020(3)	$B_{33}=(c^{*2}/a^{*2})B_{11}$				
F(5)	0·0484(9)	0·1677(10)	0·479(3)	0·0018(2)					
Li	0·068(30)	0·163(30)	0·773(8)	0·0015(8)					

Table 2. *Interatomic distances in* $LiUF_5$

Bond	*d*	$\sigma(d)$	Bond	*d*	$\sigma(d)$
U–F(2)	2·26 Å	0·02 Å	Li–F(1)	1·84 Å	0·05 Å
U–F(5)	2·26	0·02	Li–F(5)	1·95	0·06
U–F(4)	2·27	0·02	Li–F(5)	2·02	0·05
U–F(3)	2·30	0·01	Li–F(3)	2·09	0·06
U–F(4)	2·31	0·02	Li–F(2)	2·12	0·05
U–F(1)	2·31	0·02	Li–F(5)	2·31	0·05
U–F(3)	2·34	0·01			
U–F(1)	2·47	0·02			
U–F(2)	2·59	0·02			
Nonbonded contacts			Nonbonded contacts		
F(1)–F(1)	2·51	0·03	F(2)–F(4)	2·93	0·02
F(1)–F(3)	2·59	0·02	F(2)–F(5)	3·03	0·02
F(1)–F(4)	2·78	0·02	F(2)–F(5)	3·13	0·02
F(1)–F(2)	2·81	0·02	F(3)–F(5)	2·65	0·02
F(1)–F(3)	2·83	0·02	F(3)–F(4)	2·71	0·02
F(1)–F(4)	2·90	0·02	F(3)–F(3)	2·76	0·02
F(1)–F(5)	2·91	0·02	F(3)–F(3)	2·76	0·02
F(1)–F(3)	2·94	0·02	F(3)–F(5)	2·80	0·02
F(1)–F(2)	3·01	0·02	F(4)–F(4)	2·71	0·02
F(1)–F(5)	3·11	0·02	F(4)–F(4)	2·71	0·02
F(1)–F(2)	3·25	0·02	F(4)–F(5)	2·71	0·02
F(2)–F(2)	2·53	0·03	F(5)–F(5)	2·78	0·03
F(2)–F(3)	2·56	0·02	F(5)–F(5)	2·78	0·03
F(2)–F(5)	2·64	0·02	F(5)–F(5)	2·84	0·03
F(2)–F(4)	2·92	0·02			

Table 3. *Observed and calculated structure factors for* $LiUF_5$

L	FOBS	FCAL
	0 0 L	
4	1055	977
8	604	676
	0 1 L	
1	220	-240
3	97	-57
5	50	-150
7	0	26
	0 2 L	
0	0	-48
2	794	-774
4	0	-52
6	596	-539
8	0	25
	0 3 L	
1	538	-564
3	585	602
5	395	-378
7	328	295
	0 4 L	
0	94	76
2	118	-29
4	64	68
6	68	-75
	0 5 L	
1	560	-507
3	626	633
5	411	-427
7	386	374
	0 6 L	
0	185	231
2	658	665
4	167	186
6	390	438
	0 7 L	
1	227	-213
3	214	204
5	312	-338
7	60	103
	0 8 L	
0	1187	-1278
2	90	-45
4	835	-875
6	34	29
	0 9 L	
1	0	21
3	124	116
5	37	40
7	26	16
	0 10 L	
0	123	-132
2	808	731
4	86	-72
6	560	549
	0 11 L	
1	304	313
3	316	-331
5	260	264
	0 12 L	
0	234	-264
2	169	166
4	145	-157
6	108	125
	0 13 L	
1	444	425
3	454	-464
5	308	326
	0 14 L	
0	140	-212
2	419	-413
4	168	-178
	0 15 L	
1	300	287
3	268	-288
	0 16 L	
0	715	687
2	0	53
4	630	626
	0 17 L	
1	62	72
3	130	-116
	0 18 L	
0	82	104
2	519	-597
	1 1 L	
2	0	6
4	46	-22
6	19	-27
8	54	58
	1 2 L	
1	279	299
3	141	124
5	167	159
7	179	162
	1 3 L	
2	38	22
4	93	81
6	141	-136
8	11	12
	1 4 L	
1	459	-493
3	531	-531
5	505	-498
7	323	-310
	1 5 L	
2	0	9
4	55	62
6	48	4
	1 6 L	
1	393	422
3	412	434
5	323	328
7	330	314
	1 7 L	
2	67	79
4	28	-23
6	66	-32
	1 8 L	
1	231	-211
3	138	-110
5	167	-178
7	40	-45
	1 9 L	
2	85	-2
4	41	57
6	13	6
	1 10 L	
1	232	-206
3	31	-67
5	125	-136
	1 11 L	
2	0	76
4	0	-32
6	46	67
	1 12 L	
1	385	374
3	382	387
5	314	325
	1 13 L	
2	65	15
4	59	-76
	1 14 L	
1	345	-340
3	358	-360
5	243	-246
	1 15 L	
2	0	-7
4	34	23
	1 16 L	
1	187	199
3	105	120
	1 17 L	
2	0	-43
	1 18 L	
1	98	107
	2 1 L	
1	557	-571
3	538	507
5	442	-402
7	395	366
	2 2 L	
0	726	749
2	546	510
4	529	504
6	410	383
8	399	356
	2 3 L	
1	540	-635
3	547	530
5	436	-438
7	296	288
	2 4 L	
0	736	-727
2	55	65
4	556	-540
6	65	-64
	2 5 L	
1	215	-226
3	301	310
5	278	-277
7	201	207
	2 6 L	
0	421	-408
2	547	573
4	423	-457
6	387	379
	2 7 L	
1	97	98
3	117	-91
5	79	52
7	37	-13
	2 8 L	
0	122	-108
2	809	791
4	102	-102
6	607	611
	2 9 L	
1	301	291
3	297	-313
5	266	268
7	294	-298
	2 10 L	
0	671	-627
2	297	-288
4	505	-533
6	253	-250
	2 11 L	
1	497	474
3	447	-444
5	426	430
	2 12 L	
0	376	379
2	190	197
4	409	405
6	104	125
	2 13 L	
1	371	347
3	310	-316
5	249	249
	2 14 L	
0	325	317
2	388	-384
4	285	305
	2 15 L	
1	68	84
3	60	-52
	2 16 L	
0	44	172
2	691	-664
4	77	82
	2 17 L	
1	190	-186
3	148	173
	2 18 L	
0	536	536
2	0	-64
4	76	86
6	0	-5
8	99	105
	3 2 L	
1	129	134
3	145	148
5	156	173
7	118	110
	3 3 L	
2	40	-36
4	91	65
6	0	-38
	3 4 L	
1	155	162
3	306	335
5	108	100
7	184	176
	3 5 L	
2	47	-64
4	41	-74
6	85	-86
	3 6 L	
1	657	-699
3	449	-462
5	443	-452
7	297	-289
	3 7 L	
2	72	104
4	0	-10
6	0	118
	3 8 L	
1	484	467
3	398	423
5	326	334
7	319	313
	3 9 L	
2	91	9
4	52	-52
6	0	10
	3 10 L	
1	82	-100
3	196	-197
5	155	-154
	3 11 L	
2	101	-93
4	31	-32
6	59	53
	3 12 L	
1	247	-235
3	203	-193
5	118	-125
	3 13 L	
2	66	63
4	40	38
	3 14 L	
1	457	453
3	348	347
5	341	343
	3 15 L	
2	32	-35
4	43	-26
	3 16 L	
1	316	-317
3	326	-342
	3 17 L	
2	0	4
	3 18 L	
1	120	117
	4 1 L	
1	505	-491
3	609	572
5	479	-470
7	326	301
	4 2 L	
0	830	-812
2	196	-227
4	686	-655
6	63	-47
	4 3 L	
1	157	-180
3	291	305
5	139	-113
7	198	195
	4 4 L	
0	50	-37
2	1198	1237
4	0	-13
6	816	789
	4 5 L	
1	129	-117
3	129	-131
5	21	24
7	66	-79
	4 6 L	
0	970	-938
2	106	115
4	487	-478
6	119	90
	4 7 L	
1	523	512
3	339	-382
5	324	330
7	245	-245
	4 8 L	
0	221	-210
2	91	132
4	173	-171
6	83	73
	4 9 L	
1	495	467
3	459	-489
5	402	424
	4 10 L	
0	604	550
2	215	229
4	472	482
6	167	164
	4 11 L	
1	269	248
3	349	-330
5	204	210
	4 12 L	
0	43	42
2	867	-819
4	45	-12
	4 13 L	
1	70	95
3	66	-61
5	83	98
	4 14 L	
0	726	683
2	113	-114
4	534	515
	4 15 L	
1	261	-253
3	201	192
	4 16 L	
0	281	277
2	212	-210
	4 17 L	
1	355	-364
	4 18 L	
0	256	-274
2	207	227
4	46	-2
6	158	-151
	5 2 L	
1	339	-372
3	407	-406
5	370	-377
7	241	-259
	5 3 L	
2	59	45
4	31	-10
6	63	-20
	5 4 L	
1	22	-29
3	165	135
5	69	60
7	114	123
	5 5 L	
2	0	38
4	0	12
6	36	16
	5 6 L	
1	162	172
3	266	279
5	197	201
7	198	198
	5 7 L	
2	86	14
4	77	-72
6	76	41
	5 8 L	
1	489	-495
3	394	-426
5	345	-363
7	349	-337
	5 9 L	
2	0	-64
4	46	-32
6	107	111
	5 10 L	
1	321	301
3	337	320
5	352	366
	5 11 L	
2	0	-47
4	48	10
6	14	-3
	5 12 L	
1	0	-110
3	155	-144
5	55	-62
	5 13 L	
2	23	-26
4	31	-6
	5 14 L	
1	147	-169
3	180	-183
	5 15 L	
2	0	4
4	62	38
	5 16 L	
1	389	376
3	260	274
	5 17 L	
2	48	-35
	6 1 L	
1	187	-203
3	295	299
5	218	-201
7	161	144
	6 2 L	
0	458	-449
2	641	613
4	377	-390
6	401	417
	6 3 L	
1	122	132
3	126	-97
5	0	53
7	106	-106
	6 4 L	
0	1008	-954
2	39	-33
4	622	-637
6	0	4
	6 5 L	
1	554	543
3	298	-310
5	368	378
7	271	-261
	6 6 L	
0	256	276
2	610	648
4	284	307
6	440	440
	6 7 L	
1	507	502
3	413	-452
5	345	353
7	354	-344
	6 8 L	
0	74	-72
2	454	-458
4	0	-14
6	335	-340
	6 9 L	
1	337	332
3	304	-305
5	249	253
	6 10 L	
0	424	420
2	509	-487
4	303	323
6	334	-318
	6 11 L	
1	49	-37
3	53	-32
5	110	96
	6 12 L	
0	800	747
2	65	-46
4	702	686
	6 13 L	
1	300	-281
3	199	188
5	227	-236
	6 14 L	
0	195	-192
2	576	-548
4	157	-153
	6 15 L	
1	394	-382
3	373	370
	6 16 L	
0	202	196
2	239	251
	6 17 L	
1	289	-297
2	68	30
4	0	31
6	22	40
	7 2 L	
1	584	643
3	543	540
5	403	396
7	382	372
	7 3 L	
2	61	-9
4	76	-109
6	32	-48
	7 4 L	
1	452	-447
3	401	-422
5	318	-328
7	246	-233
	7 5 L	
2	56	15
4	0	40
6	49	113
	7 6 L	
1	91	67
3	153	191
5	73	70
7	18	24
	7 7 L	
2	46	45
4	30	-15
6	19	21
	7 8 L	
1	287	274
3	211	236
5	263	260
	7 9 L	
2	65	12
4	0	-94
6	34	-33
	7 10 L	
1	519	-479
5	394	-308
	7 11 L	
2	0	19
4	89	89
	7 12 L	
1	383	366
3	301	285
5	297	298
	7 13 L	
2	85	-59
4	0	22
	7 14 L	
1	75	-91
3	67	-82
	7 15 L	
2	0	-37
	7 16 L	
1	244	-238
	8 1 L	
1	176	192
3	79	-68
5	95	88
7	8	-37
	8 2 L	
0	136	-135
2	575	539
4	136	-152
6	414	417
	8 3 L	
1	469	485
3	429	-444
5	332	335
7	275	-262
	8 4 L	
0	70	92
2	204	198
4	94	27
6	195	200
	8 5 L	
1	457	457
3	468	-481
5	377	393
7	375	-369
	8 6 L	
0	264	-257
2	611	-618
4	217	-219
6	495	-506
	8 7 L	
1	223	218
3	207	-224
5	265	282
	8 8 L	
0	994	915
2	82	-41
4	766	788
6	48	-35
	8 9 L	
1	59	41
3	95	-61
5	53	16
	8 10 L	
0	184	179
2	584	-556
4	161	181
	8 11 L	
1	292	-267
3	330	308
5	246	-248
	8 12 L	
0	155	154
2	299	-285
4	64	54
	8 13 L	
1	431	-419
3	411	396
	8 14 L	
0	257	247
2	391	387
4	228	239
	8 15 L	
1	279	-275
3	280	278
	8 16 L	
0	635	-617
2	38	-15
	9 1 L	
2	44	-5
4	0	-75
6	0	16
	9 2 L	
1	371	-374
3	229	-211
5	261	-241
7	192	-188
	9 3 L	
2	0	35
4	56	-42
6	89	105
	9 4 L	
1	444	450
3	442	441
5	433	446
	9 5 L	
2	0	26
4	40	-48
6	0	5
	9 6 L	
1	228	-228
3	306	-326
5	235	-252
	9 7 L	
2	103	-107
4	42	-4
6	39	32
	9 8 L	
1	67	46
3	0	22
5	78	86
	9 9 L	
2	0	2
4	0	22
	9 10 L	
1	316	297
3	197	191
5	203	208
	9 11 L	
2	44	-51
4	17	13
	9 12 L	
1	376	-353
3	366	-364
	9 13 L	
2	55	-17
4	61	62
	9 14 L	
1	260	255
3	271	281
	9 15 L	
2	59	38
	9 16 L	
1	42	-59
	10 1 L	
1	417	418
3	511	-500
5	327	319
	10 2 L	
0	749	-744
2	343	-353
4	409	-403
6	261	-257
	10 3 L	
1	450	455
3	348	-352
5	386	382
	10 4 L	
0	507	478
2	118	-105
4	433	436
6	72	-57
	10 5 L	
1	256	244
3	304	-314
5	218	234
	10 6 L	
0	522	505
2	300	-313
4	482	504
6	234	-228
	10 7 L	
1	96	-84
3	0	-21
5	28	-46
	10 8 L	
0	90	-65
2	790	-768
4	37	-10
	10 9 L	
1	325	-291
3	314	330
5	204	-204
	10 10 L	
0	711	663
2	212	208
4	466	464
	10 11 L	
1	442	-414
3	307	313
	10 12 L	
0	290	-275
2	72	-77
4	303	-290
	10 13 L	
1	341	-325
3	278	304
	10 14 L	
0	399	-396
2	196	204
	10 15 L	
1	77	-68
2	40	50
4	55	-65
6	44	10
	11 2 L	
1	60	-64
3	7	20
5	47	25
	11 3 L	
2	0	57
4	38	-18
6	46	17
	11 4 L	
1	269	-286
3	339	-336
5	188	-196
	11 5 L	
2	66	-35
4	9	25
6	91	86
	11 6 L	
1	500	450
3	418	427
5	451	446
	11 7 L	
2	111	-82
4	46	7
	11 8 L	
1	322	-305
3	267	-266
5	208	-220
	11 9 L	
2	71	-37
4	55	50
	11 10 L	
1	0	22
3	44	33
	11 11 L	
2	37	11
4	0	15
	11 12 L	
1	312	291
3	235	246
	11 13 L	
2	45	-40
	11 14 L	
1	357	-345
	12 1 L	
1	473	447
3	365	-334
5	384	367
	12 2 L	
0	685	678
2	181	188
4	696	634
6	104	108
	12 3 L	
1	250	251
3	239	-233
5	141	139
	12 4 L	
0	40	26
2	845	-802
4	0	65
	12 5 L	
1	30	-25
3	58	60
5	49	-46
	12 6 L	
0	528	515
2	250	-255
4	411	415
	12 7 L	
1	381	-367
3	290	304
5	216	-227
	12 8 L	
0	310	294
2	30	10
4	282	281
	12 9 L	
1	438	-425
3	339	349
	12 10 L	
0	553	-514
2	227	-226
4	455	-438
	12 11 L	
1	276	-263
3	265	264
	12 12 L	
0	85	-41
2	666	633
	12 13 L	
1	65	-76
	12 14 L	
0	445	-452
2	47	-23
4	20	33
	13 2 L	
1	249	225
3	255	238
5	238	239
	13 3 L	
2	61	11
4	0	4
	13 4 L	
1	0	50
3	0	35
5	56	48
	13 5 L	
2	56	-16
4	33	-8
	13 6 L	
1	296	-295
3	323	-323
5	200	-210
	13 7 L	
2	0	14
4	76	84
	13 8 L	
1	396	402
3	364	369
	13 9 L	
2	0	-21
4	18	14
	13 10 L	
1	213	-226
3	207	-205
	13 11 L	
2	7	-8
	13 12 L	
1	0	-25
	14 1 L	
1	193	194
3	199	-194
5	196	201
	14 2 L	
0	232	249
2	565	-535
4	197	197
	14 3 L	
1	114	-94
3	83	64
5	52	-35
	14 4 L	
0	797	725
2	106	86
4	638	612
	14 5 L	
1	391	-385
3	251	266
	14 6 L	
0	202	-201
2	510	-493
4	164	-173
	14 7 L	
1	324	-337
3	396	380
	14 8 L	
0	39	-14
2	293	303
4	66	-70
	14 9 L	
1	296	-292
3	246	254
	14 10 L	
0	192	-201
2	474	474
	14 11 L	
1	0	-16
	14 12 L	
0	650	-656
2	31	-12
4	0	-23
	15 2 L	
1	426	-405
3	443	-419
	15 3 L	
2	44	-44
4	0	47
	15 4 L	
1	238	221
3	229	220
	15 5 L	
2	0	-30
4	0	20
	15 6 L	
1	72	73
3	43	22
	15 7 L	
2	0	-36
	15 8 L	
1	289	-288
3	282	-278
	15 9 L	
2	0	-14
	15 10 L	
1	337	344
	16 1 L	
1	146	-139
3	76	89
	16 2 L	
0	227	249
2	336	-341
4	237	246
	16 3 L	
1	354	-348
3	258	258
	16 4 L	
0	162	-182
2	297	-286
	16 5 L	
1	343	-343
3	370	372
	16 6 L	
0	262	246
2	553	531
	16 7 L	
1	243	-252
	16 8 L	
0	593	-586
2	42	48
	16 9 L	
1	24	-26
2	63	-31
	17 2 L	
1	293	300
3	265	275
	17 3 L	
2	48	-54
	17 4 L	
1	373	-375
2	0	-12
	17 6 L	
1	152	165
	18 1 L	
1	275	-292
	18 2 L	
0	394	379
1	332	-344
	18 4 L	
0	239	-249

$$\sigma^2(F_o^2) = [T + B + 0{\cdot}0009(T-B)^2]/[A(\mathrm{Lp})^2]$$

was used to estimate the variance in this case, where $1/[A(\mathrm{Lp})^2]$ is a factor used in converting counts to structure factors (Lp = Lorentz-polarization, A = absorption factor), T = total and B = background counts (Busing & Levy, 1957).

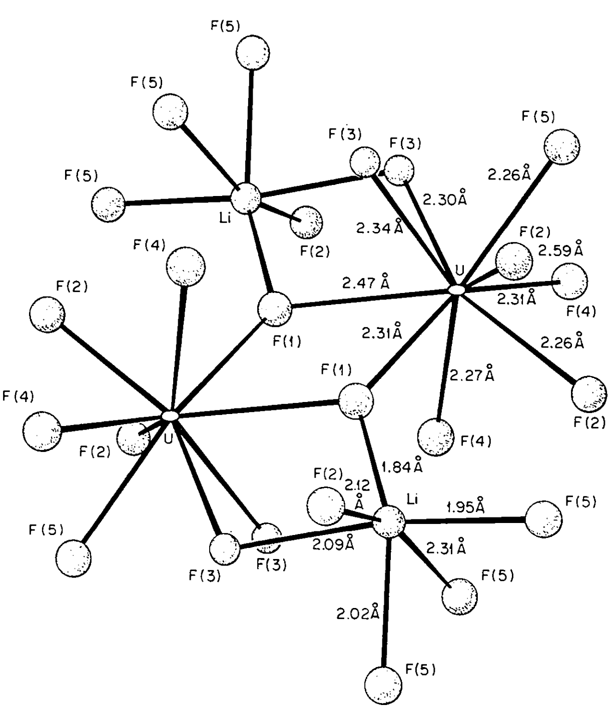

Fig. 2. Two centrosymmetrically related asymmetric units of $LiUF_5$. (In order to get maximum separation of the atoms, the unit was rotated 60° counter-clockwise around y and 6° clockwise around x. The pivot point was the symmetry center ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), and the starting orientation was the conventional cartesian system with x and y in the plane of the illustration and z out toward the viewer as in Fig. 1.)

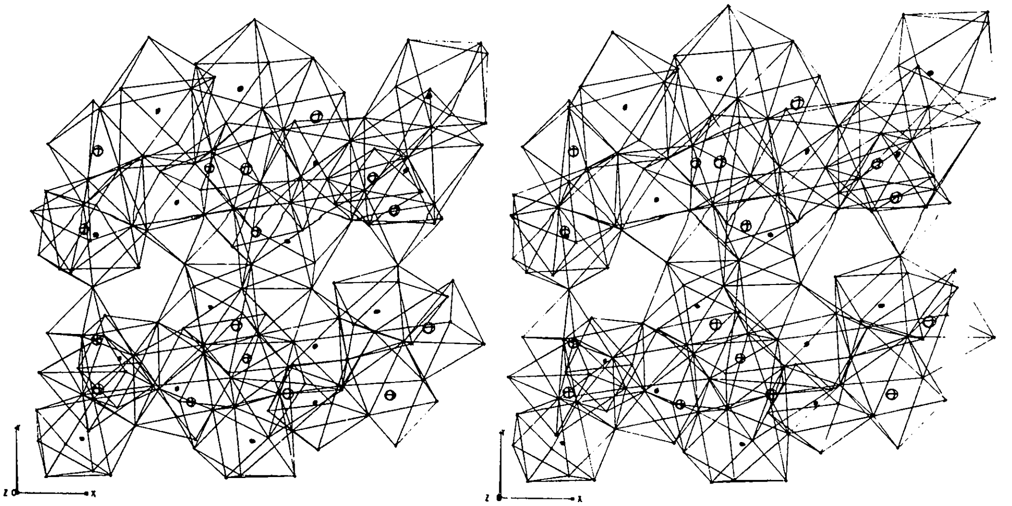

Fig. 1. Stereoscopic view down the z axis of one unit cell of $LiUF_5$.

The atomic parameters and temperature factors for $LiUF_5$ are listed in Table 1, the interatomic distances in Table 2, and the observed and calculated structure factors in Table 3. The discrepancy index $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ is 0·072 for all reflections and 0·060 for 651 measured reflections greater than σ. The standard deviation of an observation of unit weight, $[\Sigma w(F_o-F_c)^2/(n_o-n_v)]^{\frac{1}{2}}$ is 2·13 where n_o is the number of reflections and n_v the number of variables.

Discussion

Fig. 1 is a stereoscopic pair of drawings showing the contents of a unit cell. The lines are drawn between the fluoride ions forming the corners of polyhedra surrounding the uranium and lithium ions. The $9F^-$ ions surrounding each U^{4+} form the corners of a 14-faced polyhedron which is approximately a triangular prism with a pyramid on each of the three prism faces. This polyhedron is different from the two 8-cornered polyhedra found in UF_4 by Burbank (1951) and by Larson, Roof & Cromer (1964), but similar to those described for U_2F_9 by Zachariasen (1949).

The six F^- ions surrounding Li^+ form the corners of an irregular octahedron. There are sixteen crystallographically equivalent U^{4+} and Li^+ polyhedra. Each U^{4+} polyhedron shares edges with two other U^{4+}polyhedra and an Li^+ octahedron; corners with four U^{4+} polyhedra and two Li^+ octahedra and a face with an Li^+ octahedron. Each Li^+ octahedron shares edges with three Li^+ octahedra and a U^{4+} polyhedron; corners with two U^{4+} polyhedra and a face with a U^{4+} polyhedron. Fig. 2 is an illustration of two centrosymmetrically related asymmetric units of $LiUF_5$.

References

Barton, C. J., Friedman, H. A., Grimes, W. R., Insley, H., Moore, R. E. & Thoma, R. E. (1958). *J. Amer. Ceram. Soc.* **41**, (2), 63.

Burbank, R. D. (1951). USAEC Report No. K-769, Oak Ridge, Tennessee.

Burns, J. H., Ellison, R. D. & Levy, H. A. (1966). In the press.

Busing, W. R. & Levy, H. A. (1957). *J. Chem. Phys.* **26**, 563.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). USAEC Report ORNL TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

Harris, L. A. (1958). USAEC Report ORNL-CF-58-3-15. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Harris, L. A., White, G. D. & Thoma, R. E. (1959). *J. Phys. Chem.* **63**, 1974.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Larsen, E. S. & Berman, H. (1934). *The Microscopic Determination of Nonopaque Minerals.* 2nd ed. U.S.G.S. Bulletin 848.

Larson, A. C., Roof, R. B. Jr. & Cromer, D. T. (1964). *Acta Cryst.* **17**, 555.

Johnson, C. K. (1965*a*). Unpublished CDC 1604 computer program.

Johnson, C. K. (1965*b*). USAEC Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Roof, R. B. Jr. (1961). *Acta Cryst.* **14**, 934.

Thoma, R. E., Insley, H., Landau, B. S., Friedman, H. A. & Grimes, W. R. (1958). *J. Amer. Ceram. Soc.* **41**, (12), 538.

Thoma, R. E. (1962). *Inorg. Chem.* **1**, 220.

Thoma, R. E. (1965). Personal communication.

Weaver, C. F., Thoma, R. E., Insley, H. & Friedman, H. A. (1960). *J. Amer. Ceram. Soc.* **43**, (4), 213.

Zachariasen, W. H. (1949). *Acta Cryst.* **2**, 390.