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The Crystal Structure of Potassium Enneafluorothorate*

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The crystal structure of the β form of potassium enneafluorothorate, K_5ThF_9, has been determined from counter measurements of 1198 reflections and refined by full-matrix least-squares to an R index of 1·8%. The space group is $Cmc2_1$ (No. 36) with cell constants $a=7{\cdot}848$ (2), $b=12{\cdot}840$ (2) and $c=10{\cdot}785$ (3); $Z=4$, $d_{calc}=3{\cdot}66$ g.cm^{-3}. The coordination number of thorium is eight (instead of the possible nine) and the coordination polyhedron of thorium is an irregular dodecahedron with triangular faces. The average Th–F distance is 2·33 Å. The ninth fluorine atom is surrounded by six potassium atoms approximately at the corners of an octahedron and is 4·53 Å from the nearest thorium atom.

Introduction

Two polymorphs of the compound K_5ThF_9 were identified in the thorough phase study of the KF–ThF_4 system by Asker, Segnit & Wylie (1952). The compound is of interest from a structural chemistry point of view because K_5ThF_9 is one of the rare compounds having a value of nine for the ratio of monatomic unidentate ligand to central atom, others being K_2ReH_9 (Abrahams, Ginsberg & Knox, 1964; Knox & Ginsberg, 1964); and K_2TcH_9 (Ginsberg, 1964). Further, thorium(IV), being the largest of the plus-four actinides, favors nine-coordination with fluorine, the smallest of the halide ions; several examples of this behavior are known: $(NH_4)_4ThF_8$ (Penneman, Ryan & Rosenzweig, 1968; Ryan, Penneman & Rosenzweig, 1969); $(NH_4)_3ThF_7$ (Penneman & Ryan, 1970); and $(Na,Li)_7Th_6F_{31}$ (Brunton & Sears, 1969). The possibility of the existence of a discrete $ThF_9{}^{5-}$ anion prompted a full three-dimensional X-ray investigation.

Experimental

Single crystals of this material were prepared as follows: a mixture containing slightly greater than a 5: 1 mole ratio of potassium and thorium chlorides was converted to fluorides with aqueous (48%) HF followed by heating in F_2 gas overnight at 400 °C. The resulting white powder was melted in a covered platinum dish, cooled and ground, and then held at 600 °C (just below the α–β transition temperature at 635 °C) for 100 hr. The hygroscopic β-K_5ThF_9 crystals were pried from the mass, freed of any adhering KF and sealed in glass capillaries. Although the crystal faces were poorly developed the optical characteristics matched those given for K_5ThF_9 by Asker *et al.* (1952). A fragment of roughly the shape of a parallelepiped with approximate dimensions of $0{\cdot}2\times0{\cdot}2\times0{\cdot}12$ mm was selected for data collection.

Precession photographs taken with Mo $K\alpha$ radiation showed orthorhombic symmetry with the following systematic extinctions: hkl, $h+k$ odd; $h0l$, l odd. The space group is therefore $Cmcm$, $C2cm$, or $Cmc2_1$. The cell parameters were estimated by least-squares from room temperature measurements on 12 high-order reflections and are: $a=7{\cdot}848$ (2), $b=12{\cdot}840$ (2), and $c=10{\cdot}785$ (3) Å where the numbers in parentheses are the least-squares standard deviations and refer to the last digit. These cell constants are in agreement with those of Zachariasen (1948). For $Z=4$, $d_{calc}=3{\cdot}66$ g.cm^{-3}, in good agreement with the measured value of 3·60 g.cm^{-3} (Asker *et al.*, 1952).

Intensity measurements were made on hkl and $\bar{h}\bar{k}\bar{l}$ planes using a Picker computer-controlled four-circle diffractometer described by Busing, Ellison, Levy, King & Roseberry (1967). Zr-filtered Mo $K\alpha$ radiation, θ–2θ scan, bisecting positions and a take-off angle of 5°, were used to collect data on all reflections for which $2\theta\le50°$. Of the 1198 reflections measured, 1164 were judged to be observed according to the criterion $[T-KB]\ge3\sigma(I)$ where $\sigma(I)=(T+KB)^{1/2}$, T is the total count and KB is the normalized background.

The intensity of a standard reflection, sampled after every 25 reflections, showed a small but significant decrease, its final value being approximately 2·5% less than its original value. The crystal was checked periodically for orientation and centering. Multiplicative correction factors for the data were derived by fitting the standard reflection measurements with a sixth order polynomial.

Scans about three reflections on a reciprocal lattice vector near a χ angle of 90° were used to estimate an empirical absorption curve as a function of φ for three 2θ values. The absorption was taken to be the product of the value determined as above and a spherical absorption correction. The computed relative transmission varied by about 40 per cent over the range of diffractometer settings used.

Structure determination and refinement

Calculated values of $\bar{E}$ (0·91) and $\overline{E^2-1}$ (0·65) indicated the structure to be non-centric. The thorium atom posi-

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tion was determined from the Patterson function. A difference Fourier synthesis, phased on the thorium atoms, computed in the centric space group showed the potassium positions to be nearly centrically related, one in the special position 4(*c*) and one in a general position. The potassium peak on the mirror at $z=\frac{1}{4}$ was greatly elongated in the *z* direction and the contours corresponding to the potassium atom in the general position showed two maxima with approximately the same *x* and *y* coordinates, but slightly different *z* coordinates. These observations prompted us to attempt a solution to the structure in the space group $Cmc2_1$. If one chooses the first potassium position to be slightly on one side of the now pseudo mirror at $z=\frac{1}{4}$ (specifying the enantiomorph) one must still put the remaining potassium atoms in two of the four positions possible from the difference map. There are four possibilities, two of which can be rejected because of the proximity of the peaks. Both of these possible heavy atom structures converged to the same least-squares model which was then used to phase an observed Fourier synthesis. This procedure failed to distinguish the real peak from the pseudo peak for those fluorine atoms for which the *z* coordinate was near 0·25 [*i.e.* F(3) and F(7)]. It was possible, however, to pick the correct peaks from packing considerations.

A full-matrix least-squares refinement was carried out, including anisotropic temperature factors and extinction, on all reflections observed according to the criterion $I \geq 3\sigma(I)$. The quantity minimized was $\sum\omega(F_o - F_c^*)^2$ where ω is the weight based on counting statistics (Evans, 1961), and

$$F_c^* = KF_c/\{1+g\mathrm{Lp}\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right] F_c^2\}^{1/2},$$

in which K = scale constant, g = extinction correction (Zachariasen, 1963; Larson, 1967), Lp = Lorentz–polarization factor, and F_c = structure factor calculated in the usual way. Form factors used were those of Cromer & Waber (1965) for the thorium atoms; the potassium and fluorine form factors were taken from *International Tables for X-ray Crystallography* (1962) and the dispersion terms for potassium and thorium were from Cromer's (1965) work.

The model chosen as explained above refined to an unweighted *R* value of 1·8 %. The low *R* value and the physically reasonable anisotropic temperature factors were taken as proof that the model and choice of space group were correct. Hamilton's (1965) tests on the sum of the squares of the residuals, reject the hypothesis that extinction is not present as well as the hypothesis that only the heavy atoms vibrate anisotropically, at the 0·005 confidence level. The hypothesis that the choice of enantiomorph is incorrect can also be rejected at the 0·005 confidence level.

The final coordinates and anisotropic temperature factors are given in Tables 1 and 2. Table 3 contains calculated and observed structure factors.

Table 1. *Fractional atomic coordinates*

The numbers in parentheses are the least-squares standard error and refer to the least significant digits.

	x	*y*	*z*
Th	0	0·16186 (3)	0·25
K(1)	0	0·5769 (2)	0·2134 (3)
K(2)	0·2588 (4)	0·8642 (2)	0·0527 (2)
K(3)	0·2468 (4)	0·8933 (2)	0·4013 (2)
F(1)	0	0·0397 (4)	0·4054 (7)
F(2)	0	0·2033 (6)	0·0414 (8)
F(3)	0	0·3475 (4)	0·2250 (8)
F(4)	0	0·2476 (6)	0·4476 (9)
F(5)	0	0·5167 (6)	0·4619 (6)
F(6)	0·1829 (6)	0·0327 (3)	0·1780 (5)
F(7)	0·2743 (5)	0·2194 (3)	0·2729 (9)

Discussion

Fig. 1 is a stereo-pair view of the structure down the *a* axis. The thorium atom is surrounded by eight fluorine atoms instead of nine. The coordination of the fluorine atoms about the thorium atom can best be described as a slightly distorted dodecahedron with triangular faces (ideal symmetry D_{2d}). The polyhedron contains six Th–F distances of 2·31 Å (±0·02) and two of 2·40 Å. The qualitative features of the distortion of the polyhedron can be understood by inspection of the distances (Table 4) and Figs. 2 and 3 which show the coordination polyhedron and its immediate environment. The two longest Th–F contacts can be partially accounted for by the close approach to the thorium atom

Table 2. *Thermal parameters* ($\times 10^4$) *defined as*
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th	53·8 (6)	20·6 (2)	34·0 (4)	0	0	−0·9 (11)
K(1)	71 (4)	42 (2)	79 (5)	0	0	−21 (4)
K(2)	106 (4)	33 (2)	60 (2)	−4 (4)	−39 (6)	−2 (3)
K(3)	107 (4)	30 (1)	67 (2)	4 (5)	20 (7)	−7 (3)
F(1)	163 (15)	20 (4)	76 (8)	0	0	9 (10)
F(2)	154 (16)	28 (5)	23 (7)	0	0	7 (11)
F(3)	110 (10)	25 (3)	61 (12)	0	0	8 (11)
F(4)	164 (18)	25 (6)	59 (9)	0	0	−7 (11)
F(5)	94 (11)	28 (5)	59 (9)	0	0	−15 (11)
F(6)	74 (8)	36 (3)	104 (6)	10 (8)	5 (12)	−64 (7)
F(7)	59 (7)	35 (3)	172 (12)	−5 (8)	−14 (18)	−75 (11)

of the two potassium atoms nearest the two triangular faces of which the two fluorine atoms in question form an edge. This repulsive force also tends to determine which of the F–F distances are to be longer than 'contact' distances, as some of them must be, of course, since the radius ratio of Th^{4+} to F^{1-} is much larger than the 0·665 radius ratio of the ideal hard sphere model for this polyhedron type.

Table 3. *Observed and calculated structure factors*

Column headings are l, F_o/K, $\lvert F_c\rvert$.

l	F_o/K	$\lvert F_c\rvert$
H= -9 K= -3		
-3	109	107
-2	110	107
-1	-19	4
-1	-19	4
-0	107	104
H= -9 K= -1		
-3	73	72
-2	47	46
-1	85	85
-0	27	29
H= -8 K= -6		
-4	117	113
-3	67	65
-2	101	99
-1	-19	6
-0	91	92
H= -8 K= -4		
-5	74	72
-4	57	56
-3	81	79
-2	69	68
-1	94	95
-0	131	131
H= -8 K= -2		
-6	39	39
-5	87	85
-4	57	57
-3	170	169
-2	66	65
-1	101	100
-0	62	61
H= -8 K= -0		
-6	166	165
-4	130	128
-2	102	103
-0	250	228
H= -7 K= -9		
-3	54	53
-2	91	90
-1	44	43
-0	98	98
H= -7 K= -7		
-6	76	75
-5	87	85
-4	82	80
-3	94	94
-2	89	88
-1	100	98
-0	92	90
H= -7 K= -5		
-7	109	110
-6	54	53
-5	105	106
-4	54	52
-3	151	152
-2	76	76
-1	137	139
-0	79	78
H= -7 K= -3		
-8	94	93
-7	25	28
-6	117	117
-5	-19	17
-4	155	152
-3	-18	10
-2	131	134
-1	26	25
-0	174	174
H= -7 K= -1		
-8	59	56
-7	110	110
-6	65	66
-5	119	118
-4	69	67
-3	130	130
-2	54	53
-1	146	144
-0	62	61
H= -6 K=-10		
-5	59	58
-4	80	76
-3	129	128
-2	103	103
-1	76	78
-0	110	110
H= -6 K= -8		
-7	72	73
-6	81	78
-5	124	122
-4	35	30
-3	126	129
-2	30	29
-1	128	131
-0	99	100
H= -6 K= -6		
-8	124	122
-7	34	35
-6	131	131
-5	51	50
-4	118	121
-3	48	46
-2	145	145
-1	38	40
-0	158	159
H= -6 K= -4		
-9	100	99
-8	107	107
-7	76	81
-6	55	55
-5	122	120
-4	123	122
-3	111	108
-2	178	177
-1	90	89
-0	18	15
H= -6 K= -2		
-9	81	83
-8	60	61
-7	115	119
-6	67	70
-5	192	188
-4	55	55
-3	69	66
-2	45	45
-1	220	217
-0	42	38
H= -6 K= -0		
-8	139	143
-6	95	97
-4	222	220
-2	239	236
-0	162	140
H= -5 K=-11		
-5	109	110
-4	39	38
-3	108	107
-2	26	19
-1	112	113
-0	-19	20
H= -5 K= -9		
-7	27	27
-6	110	108
-5	54	55
-4	125	126
-3	50	55
-2	131	133
-1	78	81
-0	142	144
H= -5 K= -7		
-9	72	67
-8	85	83
-7	100	101
-6	93	95
-5	102	101
-4	106	108
-3	127	128
-2	150	158
-1	152	154
-0	112	113
H= -5 K= -5		
-10	43	41
-9	116	117
-8	27	31
-7	132	132
-6	65	66
-5	177	175
-4	71	69
-3	191	191
-2	82	83
-1	188	190
-0	89	88
H= -5 K= -3		
-10	109	109
-9	-21	23
-8	135	139
-7	27	25
-6	150	151
-5	18	15
-4	174	171
-3	30	26
-2	156	154
-1	20	20
-0	159	158
H= -5 K= -1		
-10	49	52
-9	114	115
-8	75	75
-7	101	102
-6	72	74
-5	167	165
-4	49	49
-3	123	122
-2	94	95
-1	141	143
-0	86	85
H= -4 K=-12		
-5	40	41
-4	125	126
-3	42	44
-2	141	144
-1	74	74
-0	97	97
H= -4 K=-10		
-8	67	68
-7	78	79
-6	87	86
-5	113	112
-4	129	127
-3	70	69
-2	115	116
-1	130	129
-0	97	98
H= -4 K= -8		
-9	88	90
-8	56	58
-7	158	159
-6	-18	10
-5	114	114
-4	60	60
-3	102	101
-2	109	110
-1	149	148
-0	20	16
H= -4 K= -6		
-10	131	133
-9	52	53
-8	118	119
-7	28	26
-6	130	129
-5	63	59
-4	194	191
-3	126	124
-2	164	163
-1	55	54
-0	145	147
H= -4 K= -4		
-11	81	79
-10	42	41
-9	102	103
-8	68	69
-7	134	136
-6	179	178
-5	124	122
-4	82	79
-3	154	156
-2	92	97
-1	194	193
-0	217	219
H= -4 K= -2		
-11	90	87
-10	76	76
-9	145	147
-8	58	55
-7	128	127
-6	76	76
-5	130	126
-4	129	126
-3	313	309
-2	114	112
-1	167	165
-0	109	109
H= -4 K= -0		
-10	126	126
-8	111	112
-6	289	287
-4	232	228
-2	171	167
-0	477	480
H= -3 K=-13		
-5	68	65
-4	77	77
-3	62	64
-2	88	90
-1	68	67
-0	82	82
H= -3 K=-11		
-7	97	98
-6	-19	12
-5	124	124
-4	-18	16
-3	134	138
-2	57	56
-1	136	139
-0	-17	6
H= -3 K= -9		
-9	54	53
-8	114	114
-7	61	62
-6	130	131
-5	51	51
-4	132	133
-3	67	65
-2	132	133
-1	60	61
-0	145	144
H= -3 K= -7		
-10	71	68
-9	85	86
-8	87	88
-7	124	120
-6	106	105
-5	132	131
-4	115	112
-3	141	140
-2	145	145
-1	138	136
-0	112	118
H= -3 K= -5		
-11	88	92
-10	42	41
-9	116	119
-8	58	56
-7	153	140
-6	87	88
-5	163	160
-4	83	83
-3	258	257
-2	103	102
-1	250	250
-0	112	113
H= -3 K= -3		
-11	-21	15
-10	137	138
-9	-19	13
-8	128	130
-7	55	56
-6	159	157
-5	30	29
H= -3 K= -3		
-4	238	232
-3	44	43
-2	220	219
-1	46	46
-0	286	292
H= -3 K= -1		
-12	46	59
-11	105	100
-10	76	77
-9	132	131
-8	97	98
-7	155	153
-6	121	122
-5	211	208
-4	112	110
-3	186	184
-2	69	68
-1	234	232
-0	46	47
H= -2 K=-14		
-4	55	55
-3	125	122
-2	27	25
-1	104	105
-0	-19	2
H= -2 K=-12		
-7	36	36
-6	121	119
-5	59	56
-4	137	138
-3	62	62
-2	133	137
-1	74	79
-0	189	195
H= -2 K=-10		
-9	79	78
-8	104	110
-7	46	46
-6	135	134
-5	69	68
-4	105	106
-3	202	205
-2	155	157
-1	127	131
-0	147	151
H= -2 K= -8		
-10	54	52
-9	132	135
-8	30	34
-7	110	112
-6	130	130
-5	194	195
-4	53	49
-3	179	176
-2	56	36
-1	155	155
-0	161	160
H= -2 K= -6		
-11	35	34
-10	96	97
-9	61	57
-8	181	181
-7	52	50
-6	195	192
-5	60	62
-4	168	166
-3	52	49
-2	215	214
-1	123	121
-0	224	225
H= -2 K= -4		
-12	78	75
-11	110	110
-10	60	61
-9	135	136
-8	150	149
-7	82	82
-6	64	59
-5	154	152
-4	199	194
-3	152	150
-2	356	347
-1	167	168
-0	24	19
H= -2 K= -2		
-12	51	50
-11	117	119
-10	63	64
-9	119	119
-8	64	64
-7	171	171
-6	73	75
-5	301	299
-4	71	72
-3	62	58
-2	82	81
-1	313	315
-0	90	94
H= -2 K= -0		
-12	98	91
-10	188	187
-8	220	222
-6	160	159
-4	336	329
-2	299	290
-0	151	154
H= -1 K=-15		
-2	102	102
-1	47	46
-0	110	109
H= -1 K=-13		
-6	80	79
-5	64	66
-4	84	85
-3	82	85
-2	84	86
-1	81	81
-0	67	65
H= -1 K=-11		
-8	30	27
-7	114	110
-6	31	25
-5	137	139
-4	37	38
-3	136	139
-2	31	30
-1	140	143
-0	-17	10
H= -1 K= -9		
-10	99	99
-9	21	23
-8	120	121
-7	47	46
-6	136	138
-5	65	64
-4	149	149
-3	77	77
-2	158	158
-1	94	100
-0	175	175
H= -1 K= -7		
-11	77	75
-10	61	61
-9	83	84
-8	97	100
-7	129	129
-6	116	115
-5	134	132
-4	132	132
-3	166	165
-2	196	195
-1	198	199
-0	135	136
H= -1 K= -5		
-12	31	28
-11	101	99
-10	46	47
-9	140	142
-8	46	46
-7	175	175
-6	92	94
-5	215	210
-4	92	92
-3	279	276
-2	119	121
-1	257	256
-0	165	163
H= -1 K= -3		
-12	98	95
-11	-21	21
-10	146	144
-9	25	25
-8	141	146
-7	45	48
-6	191	189
-5	29	30
-4	250	247
-3	57	54
-2	195	200
-1	-10	11
-0	235	247
H= -1 K= -1		
-12	74	71
-11	111	111
-10	74	71
-9	147	146
-8	100	99
-7	144	142
-6	109	107
-5	237	239
-4	64	64
-3	171	174
-2	106	112
-1	254	245
-0	110	113
H= -0 K=-16		
-5	130	126
-4	68	71
-3	110	111
-2	52	51
-1	155	134
-0	-22	13
H= -0 K=-12		
-7	97	96
-6	98	102
-5	42	41
-4	146	149
-3	44	48
-2	160	162
-1	87	86
-0	95	95
H= -0 K=-10		
-9	67	65
-8	74	74
-7	96	99
-6	93	94
-5	134	134
-4	148	147
-3	68	71
-2	144	146
-1	133	131
-0	124	129
H= -0 K= -8		
-10	23	25
-9	95	95
-8	68	68
-7	172	177
-6	18	15
-5	129	127
-4	66	64
-3	121	122
-2	141	143
-1	200	200
-0	22	33
H= -0 K= -6		
-11	46	45
-10	150	153
-9	70	77
-8	129	135
-7	46	47
-6	145	144
-5	95	92
-4	240	236
-3	156	156
-2	217	212
-1	141	141
-0	189	187
H= -0 K= -4		
-12	76	77
-11	88	90
-10	75	75
-9	125	126
-8	92	93
-7	177	178
-6	232	234
-5	170	168
-4	101	101
-3	180	177
-2	85	83
-1	160	163
-0	242	249
H= -0 K= -2		
-12	45	39
-11	105	105
-10	98	97
-9	169	170
-8	79	78
-7	142	141
-6	121	119
-5	158	136
-4	212	210
-3	397	391
-2	109	111
-1	232	220
-0	96	98
H= -0 K= -0		
-12	104	101
-12	105	101
-10	151	148
-10	152	148
-8	118	117
-8	117	117
-6	352	349
-6	351	349
-4	291	293
-4	291	293
-2	228	227
-2	228	227
0	-8	1041
2	222	231
4	268	281
6	325	334
8	131	140
10	145	146
12	93	85
H= 0 K= 2		
-12	47	39
-11	115	105
-10	103	97
-9	178	170
-8	82	78
-7	147	141
-6	121	119
-5	140	136
-4	212	210
-3	387	391
-2	104	111
-1	219	220
0	97	98
0	95	98
1	230	221
2	109	111
3	340	384
4	223	223
5	146	150
6	122	124
7	143	147
8	80	80
9	155	157
10	97	95
11	117	118
12	46	62
H= 0 K= 4		
-12	88	77
-11	102	90
-10	82	75
-9	139	126
-8	97	93
-7	185	178
-6	239	236
-5	170	168
-4	101	101
-3	175	177
-2	80	83
-1	154	163
0	243	249
0	242	249
1	172	175
2	81	80
3	201	199
4	120	120
5	170	178
6	217	219
7	184	187
H= 0 K= 4		
8	100	105
9	124	132
10	70	69
11	91	89
12	70	65
H= 0 K= 6		
-11	51	45
-10	168	155
-9	82	77
-8	138	133
-7	46	47
-6	148	144
-5	94	92
-4	235	236
-3	144	150
-2	209	212
-1	139	141
0	189	187
0	188	187
1	145	143
2	148	145
3	158	155
4	251	247
5	100	99
6	145	144
7	48	48
8	128	129
9	68	71
10	149	155
11	49	51
H= 0 K= 8		
-10	25	23
-9	99	95
-8	70	68
-7	178	177
-6	20	13
-5	125	127
-4	66	66
-3	119	122
-2	138	143
-1	197	200
0	-20	33
0	-20	33
1	221	221
2	139	140
3	114	109
4	65	63
5	113	106
6	24	25
7	182	186
8	64	65
9	98	100
10	-21	17
H= 0 K= 10		
-9	71	65
-8	72	74
-7	97	99
-6	92	94
-5	131	134
-4	148	147
-3	67	71
-2	142	140
-1	131	131
0	128	129
0	127	129
1	126	122
2	133	132
3	80	82
4	153	148
5	132	129
6	96	94
7	91	91
8	66	66
9	72	69
H= 0 K= 12		
-7	98	96
-6	100	102
-5	44	41
-4	145	149
-3	47	48
-2	160	162
-1	88	86
0	95	95
0	96	95
1	96	96
2	164	164
3	48	50
4	139	139
5	95	92
6	108	108
7	102	100
H= 0 K= 14		
-5	129	126
-4	67	71
-3	107	111
-2	51	51
-1	133	134
0	-22	13
0	-21	13
1	132	132
2	96	95
3	109	109
4	64	68
5	129	126
H= 1 K= 1		
0	112	113
1	252	245
2	112	117
3	169	176
4	73	76
5	250	233
6	104	107
7	141	146
8	108	112
9	144	146
10	75	74
11	109	109
12	77	73
H= 1 K= 3		
0	239	247
1	10	11
2	197	201
3	40	39
4	255	252
5	32	34
6	194	195
7	48	49
8	160	162
9	32	29
10	147	148
11	27	21
12	99	96
H= 1 K= 5		
0	144	143
1	250	250
2	116	114
3	281	275
4	94	91
5	214	209
6	84	83
8	46	47
9	136	137
10	42	42
11	98	95
12	30	28
H= 1 K= 7		
0	134	136
1	195	193
2	196	194
3	168	166
4	132	128
5	120	121
6	114	114
7	126	126
8	96	96
9	90	90
10	61	61
11	72	70
H= 1 K= 9		
0	176	175
1	101	102
2	162	165
3	74	71
4	130	148
5	56	56
6	143	144
7	45	44
8	124	124
9	22	17
10	102	102
H= 1 K= 11		
-8	25	27
-7	116	116
-6	23	25
-5	138	139
-4	37	38
H= 1 K= 11		
-3	136	139
-2	29	28
-1	139	145
0	-17	10
0	-17	10
1	150	152
2	30	29
3	137	137
4	41	42
5	144	144
6	22	30
7	121	120
8	23	27
H= 1 K= 13		
-6	79	79
-5	69	66
-4	84	85
-3	81	85
-2	85	86
-1	91	81
0	68	65
0	66	65
1	82	83
2	87	89
3	94	83
4	91	92
5	69	66
6	88	86
H= 1 K= 15		
-2	103	102
-1	43	46
0	111	109
0	112	109
1	39	38
2	101	103
H= 2 K= 0		
0	150	154
2	292	298
4	317	315
6	166	172
8	196	201
10	136	137
12	101	99
H= 2 K= 2		
0	91	94
1	305	313
2	73	71
3	101	104
4	63	62
5	286	287
6	67	68
7	162	164
8	66	69
9	130	136
10	61	63
11	107	104
12	52	52
H= 2 K= 4		
0	23	19
1	139	137
2	349	342
3	156	154
4	196	192
5	164	164
6	78	78
7	80	80
8	139	140
9	138	141
10	61	59
11	110	112
12	79	82
H= 2 K= 6		
0	226	225
1	122	118
2	231	230
3	56	54
4	164	161
5	60	61
6	197	195
7	28	30
8	183	184
9	64	65
10	100	99
11	33	32
H= 2 K= 8		
0	161	160
1	151	151
2	28	29
3	189	185
4	58	57
5	212	211
6	123	121
7	114	115
8	44	43
9	134	136
10	32	29
H= 2 K= 10		
0	151	151
1	128	129
2	172	175
3	200	201
4	90	87
5	69	68
6	138	137
7	96	94
8	109	112
9	74	70
H= 2 K= 12		
0	193	195
3	63	62
4	139	137
5	63	62
6	117	116
7	28	22
H= 2 K= 14		
0	-19	2
1	116	114
2	31	21
3	119	117
4	61	57
H= 3 K= 1		
0	44	47
1	238	237
2	89	89
3	189	189
4	127	150
5	209	209
6	121	125
7	154	156
8	105	107
9	126	130
10	72	75
11	98	100
12	61	60
H= 3 K= 3		
0	288	292
1	67	67
2	208	210
3	49	47
4	236	232
5	32	33
6	158	157
7	55	56
8	129	134
9	-19	16
10	138	141
11	-21	14
H= 3 K= 5		
0	114	115
1	244	244
2	103	103
3	248	247
4	88	88
5	156	153
6	84	83
7	144	141
8	59	58
9	112	115
10	58	57
11	89	93
H= 3 K= 7		
0	118	118
1	133	132
2	142	141
3	150	151
4	113	111
5	130	130
6	102	100
7	125	123
8	87	87
H= 3 K= 7		
9	83	86
10	67	66
H= 3 K= 9		
0	165	166
1	65	67
2	140	140
3	67	65
4	131	131
5	49	48
6	135	134
7	61	61
8	116	114
9	27	25
H= 3 K= 11		
0	19	6
1	143	143
2	31	33
3	128	130
4	20	16
5	126	124
6	-19	16
7	100	100
H= 3 K= 13		
0	85	82
1	67	67
2	89	89
3	64	65
4	81	79
5	68	65
H= 4 K= 0		
0	477	480
2	179	170
4	225	224
6	271	276
8	119	124
10	119	123
H= 4 K= 2		
0	108	109
1	169	167
2	109	106
3	304	305
4	136	135
5	137	137
6	77	77
7	129	130
8	59	59
9	131	135
10	75	76
11	96	98
H= 4 K= 4		
0	218	219
1	158	158
2	91	90
3	144	145
4	88	86
5	127	127
6	163	163
7	144	145
8	76	80
9	105	110
10	56	59
11	80	80
H= 4 K= 6		
0	146	147
1	58	56
2	153	151
3	124	121
4	204	202
5	66	64
6	129	131
7	29	28
8	115	117
9	49	47
10	131	136
H= 4 K= 8		
0	19	16
1	169	170
2	107	108
3	104	101
4	59	58
5	105	105
6	-18	10
7	164	166
8	52	54
9	91	91
H= 4 K= 10		
0	99	99
1	124	122
2	107	106
3	72	72
4	132	131
5	104	105
6	87	86
7	71	70
8	59	60
H= 4 K= 12		
0	96	97
1	85	81
2	144	143
3	46	44
4	117	116
5	54	51
H= 5 K= 1		
0	86	85
1	158	158
2	97	97
3	123	122
4	47	48
5	162	162
6	75	75
7	98	102
8	81	83
9	108	115
10	51	56
H= 5 K= 3		
0	160	158
1	19	18
2	158	159
3	28	27
4	173	173
5	24	20
6	153	156
7	25	27
8	130	135
9	31	27
10	107	109
H= 5 K= 5		
0	87	88
1	183	185
2	74	75
3	192	193
4	67	67
5	177	176
6	37	36
7	125	126
8	31	31
9	112	114
10	33	36
H= 5 K= 7		
0	112	113
1	150	150
2	159	158
3	129	126
4	104	104
5	92	91
6	92	94
7	96	98
8	78	79
9	71	71
H= 5 K= 9		
0	142	144
1	77	80
2	133	135
3	51	49
4	127	126
5	47	47
6	115	115
7	26	24
H= 5 K= 11		
0	24	20
1	119	121
2	22	19
3	109	108
4	45	42
5	115	115
H= 6 K= 0		
0	161	160
2	230	229
4	206	206
6	105	106
8	122	128
H= 6 K= 2		
0	41	38
1	217	215
2	54	53
3	76	76
4	62	61
5	181	178
6	70	70
7	109	113
8	42	45
9	94	96
H= 6 K= 4		
0	21	15
1	76	74
2	175	175
3	115	117
4	122	123
5	128	130
6	66	67
7	79	81
8	98	100
9	100	101
H= 6 K= 6		
0	159	159
1	40	40
2	154	154
3	53	51
4	115	116
5	53	51
6	151	152
7	34	33
8	125	127
H= 6 K= 8		
0	100	100
1	121	125
2	25	26
3	127	128
4	36	34
5	130	131
6	74	71
7	75	75
H= 6 K= 10		
0	110	110
1	82	79
2	114	113
3	127	127
4	64	61
5	61	61
H= 7 K= 1		
0	61	61
1	147	148
2	57	55
3	131	131
4	77	78
5	118	120
6	67	68
7	111	113
8	61	64
H= 7 K= 3		
0	173	176
1	28	28
2	127	132
3	-17	14
4	155	156
5	23	19
6	115	117
7	28	29
8	92	94
H= 7 K= 5		
0	79	78
1	138	139
2	77	77
3	145	146
4	52	53
5	100	103
6	48	50
7	106	105
H= 7 K= 7		
0	90	90
1	95	94
2	81	83
3	94	90
4	80	79
5	83	83
6	70	68
H= 7 K= 9		
0	98	98
1	47	45
2	95	95
3	52	49
H= 8 K= 0		
0	220	220
2	109	111
4	128	128
6	156	157
H= 8 K= 2		
0	61	61
1	100	101
2	63	60
3	164	165
4	60	60
5	89	90
6	38	39
H= 8 K= 4		
0	131	131
1	96	97
2	64	65
3	81	82
4	57	56
5	76	73
H= 8 K= 6		
0	89	92
1	-19	6
2	94	96
3	61	62
4	121	121
H= 9 K= 1		
0	31	29
1	83	81
2	54	53
3	75	76
H= 9 K= 3		
0	103	104
1	-19	2
2	107	107

Table 4. *Interatomic distances*

The associated least-squares errors are 0·010, 0·015 and 0·010 Å for Th–F, F–F, and K–F distances respectively. The numbers in parentheses preceding some distances are the multiplicities in the coordination polyhedron.

Th–F(1)	2·30 Å	K(1)–F(3)	2·95 Å
Th–F(2)	2·31	K(1)–F(5)	(2) 2·58
Th–F(3)	2·40	K(1)–F(6)	(2) 2·63
Th–F(4)	2·40	K(1)–F(7)	2·97
Th–F(6)	(2) 2·33	K(1)–F(7)	2·78
Th–F(7)	(2) 2·29		
		K(2)–F(1)	2·86
F(1)–F(4)	2·71	K(2)–F(2)	2·80
F(1)–F(5)	(2) 2·84	K(2)–F(3)	2·66
F(2)–F(3)	2·71	K(2)–F(4)	2·73
F(2)–F(6)	(2) 3·00	K(2)–F(5)	2·62
F(3)–F(4)	2·72	K(2)–F(7)	2·62
F(3)–F(6)	(2) 2·76		
F(4)–F(6)	(2) 2·88	K(3)–F(1)	2·70
F(5)–F(5)	2·87	K(3)–F(2)	2·75
F(5)–F(6)	(2) 2·70	K(3)–F(3)	2·81
		K(3)–F(4)	2·77
		K(3)–F(5)	3·17
		K(3)–F(5)	3·04
		K(3)–F(6)	2·63
		K(3)–F(7)	2·62

The fluorine atom which is not in the thorium coordination polyhedron (being 4·53 Å away from the thorium atom) is surrounded by six potassium atoms whose configuration may be described as an irregular octahedron. Two of the potassium atoms have coordination numbers of eight (*i.e.* with K–F distances less than 3·5 Å) and the remaining potassium atom has a coordination number of seven.

It is not too surprising that the coordination number of the thorium atom is not nine in K_5ThF_9 since it would be necessary for the anion to have a formal charge of minus five to accomplish this. One could reduce the charge on the anion by choosing a central actinide ion with charge plus five (such as Pa^{5+}). All such M^{5+} ions have smaller ionic radii than Th^{4+} and prefer 8-coordination, although Pa^{5+}, as the largest of the M^{5+} ions, does have 9-coordination in K_2PaF_7 (Brown, Kettle & Smith, 1967). Pa^{5+} is 8-coordinated in cubic Na_3PaF_8 (Brown, Easey & Rickard, 1969) as it also is in $RbPaF_6$ (Burns, Levy & Keller, 1968) and in $KPaF_6$ and NH_4PaF_6 (Asprey, Kruse, Rosenzweig & Penneman, 1966). Still, it might be worthwhile to look for hypothetical K_4PaF_9.

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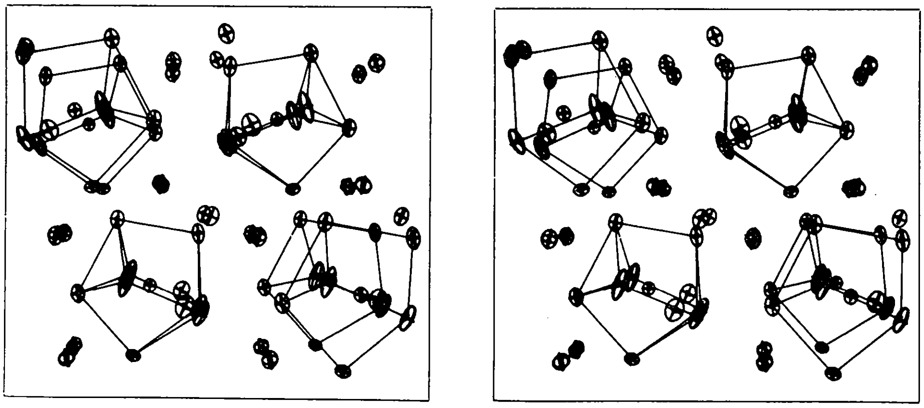

Fig. 1. Stereo-view of the structure down the *a* axis. Thermal ellipsoid axes are 3 times the root-mean-square amplitude of vibration.

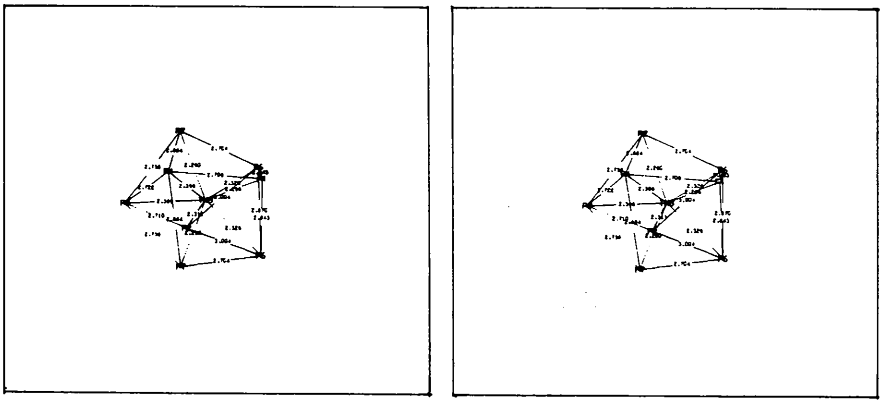

Fig. 2. Stereo-view showing F–F and Th–F distances.

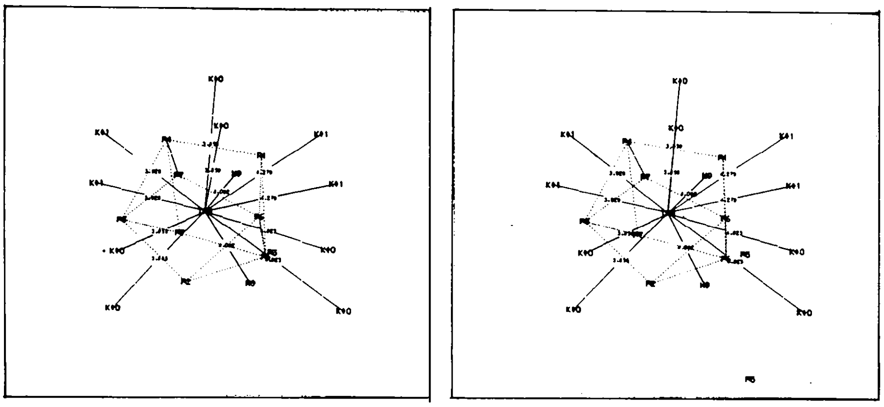

Fig. 3. Stereo-view showing Th–K distances. K(9) in this Figure corresponds to K(1) in Table 1; K(10) corresponds to K(2) and K(11) to K(3).

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Refinement of the Crystal Structure of Stilbite

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Stilbite, $Na_{1\cdot28}Ca_{4\cdot18}Mg_{0\cdot18}[Al_{10\cdot30}Si_{25\cdot71}O_{72}].34\cdot07\ H_2O$, a zeolite belonging to the heulandite group, crystallizes in the monoclinic, pseudo-orthorhombic, system, space group $C2/m$ with $a=13\cdot64$, $b=18\cdot24$, $c=11\cdot27$ Å and $\beta=128°$; $Z=1$. The structure was refined by three-dimensional electron density syntheses and least-squares to a final reliability index R of 12·3% for observed reflexions. The silicate framework can be described as consisting of a fundamental polyhedral configuration containing four- and five-membered rings of tetrahedra. In the stilbite framework there are two sets of channels, the biggest running parallel to the *a* axis, the smallest to the *c** axis. Several attempts to identify the ordering of Si and Al atoms in the framework were made and the results discussed. As in related zeolites the exchangeable cations and water molecules occur within the cavities formed by the intersecting channels. Calcium atoms have been found to be completely insulated from framework atoms by a sphere of hydration of their own. Sodium atoms lie in interstices between these spheres and the framework wall. The (010) cleavage and habit of stilbite are well explained by the small number of oxygen bridges linking the tetrahedral sheets. Explanations of the twinning are suggested.

Introduction

Stilbite is a common natural zeolite formed as a result of late-stage hydrothermal activity and it occurs mainly in cavities of basalts and in crevices of metamorphic rocks.

Gabuda, Lundin & Mikhailov (1963) investigated the position of the water molecules in stilbite by the nuclear magnetic resonance method.

The description of the unrefined framework of tetrahedra of stilbite has been given by Galli & Gottardi (1966).

The purpose of this work was to refine the structure, locate the exchangeable-cation and water-molecule positions and investigate the Si/Al distribution within the framework. The results of this research, along with derived data, are given in this report.

Experimental

The stilbite studied was from a basalt from Iceland (specimen No. 3157 of the Museo di Mineralogia dell' Università di Pisa). The crystal data used in this investigation, the same as used by Galli & Gottardi (1966) are:

$a=13\cdot64\ \pm0\cdot03$ Å,
$b=18\cdot24\ \pm0\cdot04$
$c=11\cdot27\ \pm0\cdot02$
$\beta=128°0'\pm15'$
$U=2209$ Å^3
Space group $C2/m$

In the unit cell there is one stoichiometric unit $Na_{1\cdot28}Ca_{4\cdot18}Mg_{0\cdot18}[Al_{10\cdot30}Si_{25\cdot71}O_{72}].34\cdot07H_2O$

$D_{\text{calc}}=2\cdot23$ g.cm^{-3}
D_{exp} $2\cdot19\pm0\cdot01$ g.cm^{-3}.

The experimental density was obtained with a torsion microbalance, on small splinters weighing a few milligrams.

As direction [102] is almost normal to **a**, stilbite is pseudo-orthorhombic with unit-cell dimensions

$$a=13\cdot64,\ b=18\cdot24,\ c=8\cdot88\ \text{Å};\ \beta=89°5'\ .$$

Photographic data were collected on a Weissenberg camera with equi-inclination geometry and on a Buer-