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The refinement of zinnwaldite-1*M* in subgroup symmetry

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Abstract

The structure of a zinnwaldite-1*M* from the Sadisdorf Mine, D.D.R., has been refined in *C*2/*m*, *C*2, and *C*1 symmetries. The composition is $(K_{0.90}Na_{0.05})$ $(Al_{1.05}Fe^{3+}_{0.16}Ti_{0.01}Fe^{2+}_{0.77}Mn_{0.05}Mg_{0.01}Li_{0.67})(Si_{3.09}Al_{0.91})O_{10}(OH)_{0.79}F_{1.21}$. The cell parameters are a = 5.296, b = 9.140, c = 10.096 A, and β = 100.83°. Refinement in triclinic symmetry *C*1 using the ordered-model approach gave atomic coordinates consistent with monoclinic *C*2 symmetry. In *C*2 symmetry, octahedra *M*(2) and *M*(3) related by the pseudo-mirror plane are significantly different in size (mean *M*—O,F = 1.882,2.131 A) and, to a lesser extent, in electron count (11.5 and 13.5). Octahedral Al completely occupies *M*(2), and the remaining Fe, Li, other cations, and vacancies are nearly randomly distributed over *M*(3) and the *trans* octahedron *M*(1). The (F,OH) atom has moved off the pseudo-mirror plane in order to coordinate more closely with Al in *M*(2). It is anticipated that all fluorine-rich zinnwaldites and lepidolites will have a similar ordering pattern. The *cis*-orientation of fluorine along the *M*(2):*M*(3) shared edge allows a closer F—F approach around a small cation in either site than is possible along any *M*(1) shared edge involving larger oxygen atoms. The larger *M*(1) and *M*(3) octahedra are flattened considerably (ψ = 60.8°) in order to fit onto the smaller, more regular (ψ = 56.5°) *M*(2) octahedron. The two nonequivalent tetrahedra differ slightly in size (mean *T*—O = 1.646,1.639 A), are elongate, and rotated by 5.8°.

Introduction

Zinnwaldite is a Li,Fe,Al trioctahedral mica commonly found in greisens, associated veins, and in some granites and pegmatites. It is defined by Foster (1960) as having a Li content of 1.00 ± 0.25 atoms per formula unit (~2.50–4.50 weight percent Li_2O), in contrast to protolithionite with 0.50 ± 0.25 atoms and lepidolite with >1.25 atoms. Rieder (1968, 1970*a*) and Rieder *et al.* (1971) have studied a suite of natural Li–Fe micas, from the Krušné hory Mountains (Erzgebirge) of Czechoslovakia and Germany, that lie close to the join between polylithionite and siderophyllite. As a result of this study Rieder (1970*a*) proposed broadening the composition of zinnwaldite so that it ranges from x = 1 to 3 in the series $K_2Fe^{2+}_xLi_{4-x}$ $(Al,Fe^{3+})_2(Al_xSi_{8-x})O_{20}(OH,F)_4$, where x = 0 for polylithionite and x = 4 for siderophyllite. Most of the zinnwaldites were of the 1*M* structural type (Rieder, 1970*b*).

Rieder (1968) agrees with Foster (1960) that there always is close to 1.0 small trivalent octahedral cation (Al,Fe^{3+}) per formula unit in zinnwaldite. Although the larger octahedral cations (Li,Fe^{2+},Mg,Mn) are somewhat variable in number, they never exceed 2.0. This ideal ratio of 1:2 led Rieder to postulate octahedral ordering for zinnwaldite-1*M* of the type found in clintonite-1*M* (= xanthophyllite), wherein each small *M*(1) octahedron on the mirror plane of the ideal *C*2/*m* space group is surrounded symmetrically by six larger *M*(2) octahedra in an overall 1:2 ratio. This ordering was believed to account for the observation that *d*(001) values for natural zinnwaldites are about 0.1 A smaller than for synthetic specimens, which are presumed to be disordered.

Approximately two dozen mica structures have been refined that show octahedral ordering, either of cations or, for dioctahedral compositions, of cations plus vacancies. Clintonite-1*M* (= xanthophyllite) is the only exception to the rule that the unique octahedron *M*(1) on the symmetry plane of each layer is larger than the two equivalent *M*(2) octahedra. The "normal" ordering pattern with *M*(1) larger than the average *M*(2) site has been shown to be adopted even in cases where the octahedral composition logically might suggest the reverse pattern. An example is polylithionite-1*M*, in which there are two large octahedral Li ions and one smaller Al ion. However, the ordering pattern found by Takeda and Burnham (1969) consists of one large *M*(1) octahedral site on the mirror plane with composition $Li_{0.89}Al_{0.11}$ and two smaller symmetry-related *M*(2) sites of average composition $Li_{0.55}Al_{0.45}$.

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This paper reports an X-ray refinement of one of Rieder's zinnwaldite specimens. This study was undertaken, first, to test the Rieder ordering hypothesis, because it would be of particular interest to find another exception to the prevalent ordering pattern. Second, even if the "normal" ordering pattern were to be found, the composition appears so favorable for ordering that the possibility of crystallographically-distinct *M*(2) sites should be investigated in subgroup symmetry. Refinement in subgroup symmetry has not been attempted often, but recently has been successful in showing tetrahedral ordering in margarite-$2M_1$ (Guggenheim and Bailey, 1975) and both tetrahedral and octahedral ordering in a dioctahedral 1*M* mica (Sidorenko *et al.*, 1975).

Experimental

Dr. Milan Rieder of Charles University kindly furnished a suite of analyzed zinnwaldite samples. A crystal from sample #40 from the Sadisdorf Mine dump, D.D.R., was selected as giving the sharpest reflections. The crystal is 0.4 × 0.3 × 0.05 mm and light amber in color. The composition of the crystal used for the structural analysis was determined by electron microprobe analysis (Table 1) after the completion of data collection. The Li content and the ratio of Fe^{2+} to Fe^{3+} were taken from the wet-chemical analysis data for the bulk sample as reported by Rieder (1970*a*). The resulting formula unit is $(K_{0.90}Na_{0.05})(Al_{1.05}Fe^{3+}_{0.16}Ti_{0.01}Fe^{2+}_{0.77}Mn_{0.05}Mg_{0.01}Li_{0.67}\square_{0.28})(Si_{3.09}Al_{0.91})O_{10}(OH)_{0.79}F_{1.21}$. This formula is similar to that given by the bulk analysis, except for a slightly lower Si content. Rieder *et al.* (1971) cite $2V_\alpha = 27° \pm 1°$ and the γ refractive index as 1.595 ± 0.001 for this specimen.

Unit-cell parameters of $a = 5.296(1)$, $b = 9.140(2)$, $c = 10.096(3)$ A, and $\beta = 100.83(2)°$ were determined by least-squares refinement of 15 high-angle reflections measured on a Syntex $P2_1$ autodiffractometer. Two intensity data sets were collected. First, the intensities of 2,993 non-zero reflections were measured, using graphite-monochromatized Mo*K*α radiation. The data were collected in the $2\theta:\theta$ variable-scan mode in four quadants of the limiting sphere from $2° < 2\theta < 90°$. Two standard reflections were monitored after every 50 reflections to check crystal and electronic stability. Reflections were considered as observed if $I > 2\sigma(I)$, where *I* was calculated from $I = [S - (B_1 + B_2)/B_r]T_r$, *S* being the scan count, B_1 and B_2 the background, B_r the ratio of background time to scan time, and T_r the 2θ scan rate in degrees per minute. $\sigma(I)$ was calculated from standard counting statistics. Integrated intensities were corrected for Lorentz and polarization effects, but not for absorption. This data set was used for initial refinement and for determining the best ordering models in both monoclinic and triclinic subgroup symmetry. Final refinement of the monoclinic models used a second data set of 1,550 independent non-zero intensities collected in the same manner from only two quadrants. These data were empirically corrected for absorption by comparing the data to complete ψ scans (10° increments in ϕ) for selected reflections spaced at 2θ intervals of 5°. Absorption is a major factor because of the platy nature of the crystal. A maximum intensity decrease of 49 percent was observed for some reflections during the ψ scans.

Table 1. Chemical analysis of Sadisdorf zinnwaldite

Oxide	Weight percent			Cations per 22 positive charges		
	[a]Wet	Microprobe	Best data			
SiO_2	42.86	40.70	40.70	Si	3.090	4.000^{IV}
Al_2O_3	21.89	21.95	21.95	Al	0.910	
TiO_2	0.16	0.20	0.20		1.054	
Fe_2O_3	2.78	15.04	2.85	Ti	0.011	
FeO	11.84		12.19	Fe^{3+}	0.163	
MnO	0.73	0.70	0.70	Fe^{2+}	0.774	2.721^{VI}
MgO	[b]tr	0.04	0.04	Mn	0.045	
Li_2O	2.19	[c]na	2.19	Mg	0.005	
CaO	0.51	[d]bd	0.00	Li	0.669	
Na_2O	0.26	0.36	0.36	Na	0.053	0.953^{XII}
K_2O	9.85	9.29	9.29	K	0.900	
P_2O_5	0.04	na	0.00			
H_2O^+	na	na	na			
H_2O^-	0.96	na	0.96			
F	5.20	5.67	5.67			
Sum of Oxides	99.27	93.95	97.10			

[a] *Wet chemical analysis by M. Huka and J. Obermajer, Geological Survey of Czechoslovakia, as reported by Rieder (1970a).*
[b] *Trace.* [c] *Not analyzed.* [d] *Below detection.*

Refinement

Initial atomic coordinates in the ideal space group *C*2/*m* were obtained from the structure of fluor-polylithionite (Takeda and Burnham, 1969). After several cycles of least-squares refinement with program ORFLS using the first data set with reflections from $2° < 2\theta < 55°$, scattering-factor adjustments to *M*(1) and *M*(2) were made as a result of three-dimensional electron-density difference maps. Additional least-squares refinement reduced R_1 to 12.5 percent. At this stage *M*(1) was significantly larger than *M*(2), and

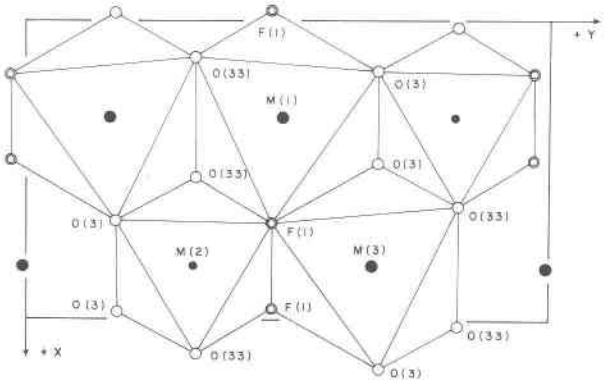

Fig. 1. Octahedral ordering pattern of Sadisdorf zinnwaldite-1*M* in subgroup *C*2.

the average (F,OH) atom had an unusually high temperature factor of 3.0 A². This is the "normal" ordering pattern, so subsequent refinement concentrated on subgroup ordering models.

Refinement in subgroup symmetry initially followed the method outlined by Guggenheim and Bailey (1975) for margarite-$2M_1$. Because of convergence problems, it is best not to start refinement in subgroup symmetry by using atomic coordinates of higher symmetry. Instead, atoms were moved away from their pseudosymmetrically-related positions by postulating an ordering scheme in subgroup symmetry that was still consistent with the parent space-group refinement. The atomic coordinates of each possible ordering model were determined from a distance-least-squares program, and those results were then refined by varying the parameters of pseudosymmetry-related positions independently. The latter precaution actually may not be necessary, since in the later stages of refinement it proved possible to vary all of the parameters together without significantly high correlations.

For subgroup *C*2, the *M*(2) site and its pseudosymmetrically-related *M*(3) site become crystallographically independent (Fig. 1). Three-dimensional electron-density difference maps at this stage indicated *M*(3) had approximately four more electrons per site than *M*(2). Only two ordered models are compatible with the average structure in the parent space group *C*2/*m*, namely *M*(2) can be smaller or larger than *M*(3). Atomic coordinates for these two models were derived, using the DLS program OPTDIS written by W. A. Dollase of the University of California at Los Angeles. Subsequent cycles of ORFLS refinement indicated the model with *M*(2) smaller than *M*(3) to be much better than the reverse model (wR = 8.9% versus 14.0%).

There is only one independent tetrahedral site in the parent space group *C*2/*m*. Although there are two independent tetrahedra in space group *C*2, mean *T*—O distances for both proved to differ by only 0.01 A, so that any ordering of Si,Al must be very small. The twofold axis passing through the 2:1 layer in space group *C*2 relates tetrahedra on one side of the octahedral sheet to tetrahedra on the other side. It is implicit in space group *C*2, therefore, that both tetrahedral sheets must be identical. To determine whether tetrahedral ordering is present in still lower symmetry or whether both tetrahedral sheets are the same in composition, four models representing all possible tetrahedral ordering patterns were postulated for triclinic *C*1 symmetry. The four models were tested with the four-quadrant intensity data of set one, and each converged back from the postulated ordered atomic coordinates to the more disordered structure of *C*2 symmetry with equivalent tetrahedral sheets. For all refinements involving noncentrosymmetric space groups, one atom was fixed in position.

Final refinement of the best *C*2 model and of the *C*2/*m* average structure was accomplished with the second data set in two stages, first using only 633 independent reflections with $2\theta \leq 55°$ from two quadrants and incorporating absorption corrections. Initially, pseudosymmetry-related atomic coordinates were varied independently in two sets until the final stages of refinement. Then a full matrix refinement was used. No significant differences in atomic positions resulted from this refinement relative to that using the first data set, so final refinement consisted primarily of adjustment of isotropic temperature factors (*B*) and of scattering factors (*f*) for the octahedral cations, as determined by alternating cycles of electron-density difference maps and least-squares refinement. The *f* and *B* values proved interrelated in that an increase of one electron in octahedral scattering power would increase *B* for that same site by approximately 0.25, and the reverse for a decrease. Refinement was terminated for both models when *f* values that gave flat difference maps also satisfied the total octahedral-site composition for half-ionized atoms and were correlated with reasonable isotropic *B* values. Unweighted *R* for the isotropic *C*2 ordered model was 6.1 percent and for the average *C*2/*m* structure was 12.2 percent at this stage. In the second stage of final refinement, both the *C*2 ordered model and the *C*2/*m* average structure were refined with anisotropic temperature factors, using the second data set out to $2\theta \leq 90°$. Fifty-seven reflections known to be associated with strong white-

Table 2. Observed and calculated structure amplitudes

H	K	10FO	10FC
L = 0			
4	0	69	55
6	0	104	105
8	0	68	58
10	0	188	178
3	1	86	85
5	1	168	171
7	1	147	151
4	2	343	341
6	2	121	121
8	2	174	169
3	3	601	568
5	3	697	695
7	3	342	349
9	3	102	103
2	4	186	175
4	4	246	247
6	4	299	293
8	4	86	84
1	5	297	255
3	5	141	137
5	5	230	231
7	5	148	145
9	5	68	41
2	6	1117	1035
4	6	137	134
6	6	65	62
8	6	129	123
1	7	303	295
3	7	80	80
5	7	158	151
7	7	85	85
0	8	141	138
2	8	58	58
4	8	279	277
6	8	190	200
8	8	60	34
1	9	287	266
3	9	396	382
5	9	382	372
7	9	248	250
9	9	139	136
0	10	111	106
2	10	165	164
4	10	193	191
6	10	151	149
8	10	113	108
1	11	281	271
3	11	174	171
5	11	138	143
7	11	84	73
2	12	422	406
4	12	118	117
6	12	67	76
1	13	127	122
3	13	79	71
5	13	123	126
7	13	89	68
0	14	208	195
4	14	159	178
6	14	115	108
1	15	127	125
3	15	135	136
5	15	237	228
2	16	70	75
4	16	110	110
1	17	149	152
3	17	68	24
0	18	282	301
L = 1			
2	0	1116	1088
4	0	723	726
-4	0	646	642
6	0	130	143
-6	0	213	215
-8	0	396	377
-10	0	177	173
-1	1	210	190
3	1	453	431
-3	1	209	196
5	1	306	310
-5	1	149	158
7	1	90	96
-7	1	81	84
9	1	95	85
-9	1	76	76
2	2	334	310
-2	2	412	380
4	2	475	491
-4	2	118	118
6	2	60	6
-6	2	174	173
-8	2	164	162
1	3	294	257
3	3	170	168
5	3	295	295
-5	3	521	518
7	3	260	275
9	3	279	284
2	4	486	435
-2	4	342	311
4	4	127	130
-4	4	204	216
6	4	187	183
-6	4	118	126
8	4	67	73
-8	4	90	91
-10	4	90	90
1	5	564	505
-1	5	239	210
3	5	308	292
-3	5	342	347
5	5	200	197
-5	5	91	97
7	5	97	94
-7	5	104	93
-9	5	77	64
-2	6	733	678
4	6	394	378
-4	6	230	230
6	6	275	268
-6	6	190	182
-8	6	237	237
1	7	196	181
-1	7	82	77
3	7	387	371
-3	7	123	125
5	7	253	244
-5	7	149	157
-7	7	112	106
9	7	68	63
-9	7	73	96
0	8	325	314
2	8	424	402
-2	8	271	258
4	8	146	141
6	8	141	126
-6	8	127	135
-8	8	95	100
1	9	192	174
-1	9	608	560
3	9	103	107
-3	9	763	736
5	9	136	143
-5	9	387	383
7	9	233	232
0	10	100	109
2	10	210	195
4	10	153	156
-4	10	128	131
-8	10	110	113
1	11	262	261
3	11	238	230
-3	11	256	244
5	11	103	93
-5	11	111	112
-7	11	124	124
0	12	204	188
-2	12	243	224
4	12	329	321
-4	12	189	187
6	12	155	158
-6	12	132	134
1	13	203	196
3	13	166	145
-3	13	121	100
5	13	112	106
-5	13	96	111
0	14	130	129
2	14	218	216
-2	14	132	119
4	14	80	80
-4	14	105	112
1	15	79	81
-1	15	302	302
3	15	90	100
-3	15	339	346
-5	15	138	129
0	16	65	66
2	16	100	90
-2	16	88	75
4	16	77	66
1	17	156	171
3	17	68	87
-3	17	186	177
0	18	70	91
L = 2			
2	0	1087	1067
-2	0	240	229
4	0	281	279
-4	0	1036	1050
6	0	440	450
-6	0	722	732
8	0	416	387
-8	0	351	330
-10	0	70	82
1	1	866	841
-1	1	680	621
3	1	450	450
-3	1	198	191
-5	1	190	195
7	1	124	122
-7	1	114	120
-9	1	65	61
4	2	188	199
-4	2	306	323
6	2	143	147
8	2	164	136
-8	2	105	101
1	3	424	391
-1	3	1111	998
3	3	249	251
5	3	64	75
-5	3	234	240
7	3	96	102
-7	3	131	128
-9	3	130	140
2	4	655	618
-2	4	225	216
-4	4	202	209
6	4	150	155
-6	4	131	126
-8	4	149	137
1	5	613	603
-1	5	510	455
3	5	357	362
-3	5	151	143
-5	5	160	170
7	5	69	76
-7	5	89	98
0	6	246	216
2	6	241	233
-2	6	180	156
4	6	409	395
-4	6	572	566
6	6	400	390
-6	6	698	703
8	6	266	271
-8	6	257	253
1	7	359	312
-1	7	443	409
3	7	184	178
-3	7	210	211
5	7	87	95
-5	7	169	168
7	7	159	146
-7	7	106	110
-9	7	76	39
0	8	256	237
2	8	238	218
-2	8	259	247
6	8	92	75
-6	8	174	180
8	8	74	71
1	9	410	386
-1	9	704	651
3	9	206	195
-3	9	216	208
5	9	110	117
-5	9	203	209
7	9	140	138
-7	9	75	59
-9	9	88	92
0	10	280	280
2	10	139	136
-2	10	216	207
4	10	81	82
-4	10	95	105
6	10	83	81
-6	10	73	61
-8	10	136	119
1	11	190	181
-1	11	399	391
3	11	106	115
-3	11	83	74
5	11	101	104
-5	11	167	162
7	11	89	69
0	12	140	141
2	12	137	142
-2	12	105	109
4	12	160	146
-4	12	402	403
6	12	268	280
-6	12	315	335
1	13	160	150
-1	13	98	82
3	13	106	70
-3	13	128	128
5	13	72	75
-5	13	74	97
-7	13	111	105
0	14	123	139
-2	14	174	174
6	14	72	47
-6	14	95	96
1	15	272	273
-1	15	227	227
3	15	162	165
-3	15	126	121
5	15	93	93
-5	15	116	115
0	16	98	105
2	16	71	73
-2	16	79	86
4	16	74	48
-1	17	114	126
-3	17	91	79
0	18	108	98
L = 3			
-2	0	401	403
4	0	125	133
-4	0	772	762
-6	0	300	313
8	0	137	129
-8	0	155	141
1	1	461	454
-1	1	849	853
3	1	103	106
-3	1	759	755
5	1	91	101
-5	1	216	211
7	1	149	155
-7	1	127	143
9	1	123	111
2	2	294	303
4	2	256	267
-4	2	268	272
6	2	59	43
-6	2	110	119
8	2	105	97
-8	2	181	166
-10	2	69	56
1	3	837	797
-1	3	1111	1041
3	3	759	752
-3	3	738	228
5	3	770	778
-5	3	215	217
7	3	322	300
-7	3	421	431
-9	3	301	314
0	4	213	200
2	4	134	131
-2	4	529	512
4	4	221	227
-4	4	237	238
6	4	113	113
-6	4	212	214
8	4	157	154
-8	4	65	76
-10	4	93	81
1	5	272	251
-1	5	461	426
3	5	71	64
-3	5	604	593
5	5	145	146
-5	5	164	165
7	5	82	62
-7	5	94	108
9	5	122	118
0	6	341	322
2	6	417	415
-2	6	793	752
4	6	172	175
-4	6	639	628
6	6	112	115
-6	6	127	123
8	6	197	200
1	7	310	303
-1	7	528	511
3	7	133	132
-3	7	360	353
-5	7	210	218
7	7	150	140
-7	7	127	127
9	7	103	82
2	8	110	110
-2	8	307	282
4	8	151	135
-4	8	251	249
6	8	111	103
8	8	108	108
-8	8	62	65
-1	9	276	266
3	9	642	628
-3	9	183	176
5	9	488	472
-5	9	122	123
7	9	176	179
-7	9	297	310
-9	9	261	263
0	10	81	83
2	10	150	149
-2	10	81	77
4	10	171	163
-4	10	88	73
-6	10	154	150
8	10	88	82
-8	10	107	105
1	11	175	182
-1	11	198	188
-3	11	193	178
5	11	85	73
-5	11	176	182
0	12	311	318
2	12	161	162
-2	12	417	390
4	12	125	134
-4	12	379	350
6	12	65	67
-6	12	85	104
1	13	107	107
-1	13	190	175
3	13	111	96
-3	13	251	240
-5	13	102	75
4	14	70	68
-4	14	123	132
6	14	97	78
-6	14	68	47
1	15	205	220
-1	15	127	129
3	15	261	279
-3	15	92	96
5	15	296	293
-5	15	128	128
2	16	70	76
4	16	98	99
-3	17	116	138
0	18	148	169
L = 4			
-2	0	743	735
4	0	810	847
-4	0	120	113
-8	0	189	174
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5	3	79	82
-5	3	114	104
-9	3	114	114
4	4	64	44
-4	4	167	171
6	4	76	70
-6	4	132	127
1	5	73	67
-1	5	127	123
3	5	92	67
-3	5	86	94
-5	5	174	156
0	6	148	142
2	6	98	98
-2	6	85	80
4	6	135	138
-4	6	292	310
-6	6	250	262
-8	6	109	99
-1	7	65	34
-3	7	132	123
5	7	105	83
-5	7	80	89
-7	7	103	107
0	8	95	88
-4	8	189	187
-6	8	121	116
1	9	333	343
-1	9	376	338
3	9	111	117
-3	9	100	93
0	10	86	88
-6	10	106	102
1	11	88	95
-1	11	103	101
3	11	67	70
-5	11	109	95
0	12	129	130
2	12	74	68
-4	12	173	166
	L = 14		
2	0	128	119
-2	0	381	381
-4	0	436	475
-6	0	68	81
1	1	115	93
-1	1	54	48
3	1	134	136
-3	1	85	92
5	1	96	97
-5	1	93	110
-2	2	94	98
4	2	104	97
-4	2	106	116
-6	2	150	141
-8	2	87	87
1	3	174	176
3	3	153	144
-3	3	159	144
5	3	144	137
-7	3	185	195
2	4	130	106
-2	4	130	110
4	4	68	57
-6	4	91	89
-8	4	84	88
1	5	129	114
3	5	131	116
-3	5	83	85
5	5	73	80
-7	5	75	74
0	6	150	149
-2	6	388	366
-4	6	294	297
-6	6	129	134
3	7	104	76
-3	7	101	90
0	8	60	51
-2	8	145	116
1	9	96	103
-1	9	78	84
3	9	101	116
-3	9	116	146
-2	10	77	41
-4	10	78	62
-6	10	129	106
-1	11	85	44
-3	11	134	108
0	12	104	99
-2	12	206	227
-4	12	203	211
	L = 15		
2	0	206	199
-2	0	177	169
4	0	161	174
1	1	151	144
-1	1	168	148
3	1	86	88
-5	1	78	66
0	2	151	138
2	2	70	50
-4	2	111	100
1	3	121	112
-1	3	180	153
-3	3	206	186
5	3	98	99
-5	3	310	324
-7	3	237	233
2	4	90	87
-4	4	94	103
-6	4	132	122
-8	4	90	80
1	5	115	103
-1	5	122	110
3	5	99	101
-3	5	70	67
-5	5	83	83
-7	5	69	60
0	6	139	157
2	6	243	228
-2	6	206	203
4	6	169	154
-6	6	72	81
1	7	129	131
-1	7	132	134
3	7	66	52
-7	7	85	63
2	8	74	73
-6	8	82	107
1	9	105	83
-1	9	70	82
3	9	77	44
-3	9	198	188
-5	9	219	234
-2	10	76	31
1	11	74	56
-2	12	134	120
	L = 16		
2	0	93	98
-2	0	111	114
4	0	308	291
-6	0	128	138
-1	1	93	98
-3	1	116	114
-5	1	61	47
-7	1	87	76
0	2	106	99
4	2	82	63
-4	2	142	111
1	3	201	202
-1	3	219	223
-3	3	172	161
-5	3	95	86
0	4	62	52
-2	4	147	137
-4	4	66	55
-1	5	81	92
-3	5	95	100
2	6	115	110
-2	6	66	45
-4	6	81	97
-6	6	116	127
3	7	85	65
-3	7	62	54
-2	8	84	66
1	9	170	170
-1	9	170	159
-3	9	139	131
-5	9	110	107
0	10	85	79
-4	10	101	76
	L = 17		
2	0	127	114
-2	0	180	176
-4	0	251	236
-6	0	115	108
3	1	81	76
-5	1	86	74
-7	1	83	69
-4	2	99	96
1	3	283	276
-1	3	70	68
3	3	231	225
2	4	64	56
-6	4	93	74
3	5	93	77
0	6	65	35
2	6	139	138
-2	6	190	170
-4	6	170	145
-6	6	153	154
-3	7	106	87
-5	7	81	72
-2	8	103	95
-1	9	104	91
	L = 18		
-2	0	291	282
-4	0	85	98
-1	1	90	88
0	2	75	70
2	2	78	53
-2	2	76	23
-4	2	74	63
-1	3	110	98
-3	3	68	26
-5	3	191	168
1	5	68	41
-1	5	87	89
0	6	239	233
-2	6	298	271
-4	6	99	102
-1	7	84	76
	L = 19		
-4	0	134	110
1	1	83	77
-5	1	71	56
-1	3	76	67
-3	3	251	230
0	4	91	94

radiation streaks were deleted from this data set for a total of 1,493 reflections. Because the octahedral coordination of the refined structure was known to be noticeably asymmetric, all of the variable parameters were varied together in one set. No significant correlation effects were indicated, and there were no significant changes in atomic coordinates. The final unweighted and weighted R values were 5.7 and 6.3 percent respectively for the $C2$ ordered model, and 12.5 and 17.4 percent for the average $C2/m$ structure. Hamilton's (1965) residual-ratio test indicates that the $C2$ model represents significant improvement over the $C2/m$ model at better than the 1 percent significance level. Tables 2–4 list observed and calculated structure amplitudes based on the anisotropic refinement results in $C2$ symmetry, final atomic coordinates, and calculated bond lengths and angles.

Tetrahedral ordering

The mean T—O bond lengths for tetrahedra $T(1)$ and $T(11)$ are 1.646 A and 1.639 A, respectively. The standard deviations of the bond lengths (Table 4) were calculated, using the correlation matrix as input to program ORFFE. The standard deviation σ_l of an individual T—O bond length is 0.004 A, the standard deviation of the mean value is $\sigma_n = \sigma_l/\sqrt{n} = 0.002$ A, and the standard deviation in their difference is $\sigma = \sqrt{2}\sigma_n = 0.0028$ A. The observed difference of 0.007 A between the two mean T—O values equals 2.50σ for this accuracy, and is just significant at the 1 percent level. From the regression analysis of Hazen and Burnham (1973) for micas, the mean T—O values correspond to tetrahedral contents of 0.233 Al and 0.190 Al in $T(1)$ and $T(11)$, respectively. This gives a total of 0.85 Al^{IV} per formula unit, in close agreement with the composition $Si_{3.09}Al_{0.91}$ determined by microprobe analysis. Thus, a small but statistically significant ordering of tetrahedral cations is indicated by the refinement.

Octahedral ordering

The most important structural feature of zinnwaldite is the unusual octahedral ordering pattern. The mean M—O,F values for $M(1)$, $M(2)$, and $M(3)$ are 2.132, 1.882, and 2.131 A, and the scattering powers are 15.0, 11.5, and 13.5 electrons, respectively. The reduction in symmetry from $C2/m$ to $C2$, therefore, is due primarily to the difference in sizes and, to a lesser extent, in scattering powers of the $M(2)$ and $M(3)$ cations across the pseudo-mirror plane (Fig. 1). $M(1)$ and $M(3)$ are identical in size and have a difference in scattering power that is probably significant.

Table 3. Final atomic parameters

Atom	x	y	z	$B_{equiv.}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	0	0.5028(2)	0	1.93	0.0181(4)	0.0048(1)	0.0054(1)	0.0	0.0013(2)	0.0
M(1)	0	-0.0069(3)	1/2	0.64	0.0067(3)	0.0009(1)	0.00236(8)	0.0	0.0013(1)	0.0
M(2)	0	0.3217(3)	1/2	0.57	0.0050(4)	0.0014(1)	0.0017(1)	0.0	0.0006(2)	0.0
M(3)	1/2	0.1631(3)	1/2	0.62	0.0050(4)	0.0012(1)	0.0023(1)	0.0	0.0000(2)	0.0
T(1)	0.0745(2)	0.1688(3)	0.2276(1)	0.52	0.0053(3)	0.0010(1)	0.0016(1)	0.0003(1)	0.0003(1)	-0.00015(7)
T(11)	0.5844(2)	0.3323(3)	0.2275(1)	0.54	0.0044(3)	0.0009(1)	0.0022(1)	0.0002(1)	0.0006(1)	-0.00003(8)
O(1)	0.0289(6)	-0.0002(5)	0.1720(3)	1.40	0.0202(9)	0.0021(2)	0.0030(2)	-0.0000(6)	0.0002(3)	-0.0002(3)
O(2)	0.3248(7)	0.2350(5)	0.1725(4)	1.42	0.0125(9)	0.0053(3)	0.0029(3)	-0.0031(5)	0.0019(4)	-0.0005(3)
O(22)	0.8177(7)	0.2641(5)	0.1597(4)	1.34	0.0117(9)	0.0046(3)	0.0031(3)	0.0028(4)	0.0010(4)	0.0007(2)
O(3)	0.1155(6)	0.1748(4)	0.3939(3)	0.71	0.0067(7)	0.0019(2)	0.0019(2)	0.0011(3)	0.0008(3)	-0.0001(2)
O(33)	0.6639(5)	0.3271(5)	0.3928(3)	0.75	0.0058(6)	0.0022(2)	0.0022(2)	0.0002(4)	0.0003(3)	0.0000(2)
F(1)	0.1089(5)	0.4715(3)	0.3989(3)	1.10	0.0108(7)	0.0025(2)	0.0032(2)	-0.0007(3)	0.0009(3)	0.0005(2)

$B_{equiv.}$ calculated from anisotropic data according to Hamilton (1959). The anisotropic temperature factor form is exp $(-\Sigma_i \Sigma_j \beta_{ij} h_j h_j)$.

The size and scattering power of *M*(2) are consistent with complete ordering of Al into this site. To a first approximation, the remaining octahedral cations and vacancies of the formula unit can be considered randomly distributed over *M*(1) and *M*(3). For this random distribution the distance of the average cation from its oxygen neighbors, neglecting the (F,OH) contacts, was calculated from the radii of Shannon and Prewitt (1969, 1970) as 2.133 A. The size of a vacancy was taken as 0.80 A in this calculation. The observed values from Table 4 are 2.133 A for mean *M*(1)—O and 2.117 A for mean *M*(3)—O. A better overall fit for calculated sizes and electron counts is obtained by moving all the smaller and lighter Al out of *M*(1) into *M*(3) and replacing with a corresponding amount of Fe^{2+}. The calculated *M*—O values then become 2.140 A for *M*(1) and 2.127 A for *M*(3), and the calculated electron counts become 13.9 and 13.1, respectively. Despite the good fit, this should not be considered a unique solution.

The (F,OH) atom has a high temperature factor ($B = 3.0$ A^2) when refined in *C*2/*m* symmetry. Figure 1 shows that in *C*2 symmetry the (F,OH) atom has moved off the mirror plane to coordinate more closely with Al in *M*(2). At the same time the equivalent isotropic *B* value for (F,OH) has decreased to 1.1 A^2 (Table 3). The *M*(3)—(F,OH) distance of 2.159 A (Table 4) is larger than the *M*(3)—O distances (2.109, 2.125 A). This octahedral irregularity, to be discussed in more detail below, was the reason for using only the oxygen contacts in calculating the octahedral cation distributions mentioned in the preceding paragraph.

The (F,OH) atom is located in the *trans*-orientation at opposite apices of the *M*(1) octahedron but in the *cis*-orientation along a shared edge between the *M*(2) and *M*(3) octahedra (Fig. 1). Because fluorine is smaller than oxygen, two (F,OH) atoms can approach each other more closely along the shared edge between *M*(2) and *M*(3) than can two oxygens along any *M*(1) shared edge. Thus, the smaller Al can be accommodated more readily in either *M*(2) or *M*(3) than in *M*(1). The small amount of tetrahedral ordering present in this crystal also favors location of a high-charge cation in *M*(2). The shared octahedral edge between *M*(2) and *M*(1) that parallels the F—F shared edge between *M*(2) and *M*(3) involves two O(3) atoms apical to *T*(1) cations in the upper and lower tetrahedral sheets (Fig. 1). Because of Al concentration in *T*(1), the apical O(3) anions are undersaturated and thus favor a trivalent cation in *M*(2). Reversal of the tetrahedral ordering pattern by placing more Al^{IV} in *T*(11) would favor octahedral Al in *M*(3) instead of *M*(2), and the particular pattern adopted may be a random choice from crystal to crystal. This also may lead to domain structures. It is anticipated that the O—H dipole will be deflected from the sheet normal to point away from *M*(2) in a direction between *M*(1) and *M*(3) and toward the undersaturated O(3)—O(3) shared edge of the next *M*(2) octahedron.

Ordering model

Rieder (1968) was correct in predicting that zinnwaldite would show octahedral ordering, although the observed ordering pattern is rotated 120° from that predicted. Rieder emphasized the smaller *d*(001) values of natural zinnwaldites relative to synthetic

Table 4. Calculated bond lengths and angles

Bond lengths (Å)				Bond angles (°)	
		Tetrahedron T(1)			
0(1)	1.646(4)	0(1)--0(2)	2.655(5)	0(1)--0(2)	107.8(2)
0(2)	1.640(4)	0(22)	2.653(5)	0(22)	107.4(2)
0(22)	1.646(4)	0(3)	2.721(4)	0(3)	111.1(2)
0(3)	1.653(4)	0(2)--0(22)	2.664(6)	0(2)--0(22)	108.3(2)
Mean	1.646	0(3)	2.727(5)	0(3)	111.8(2)
		0(22)--0(3)	2.706(5)	0(22)--0(3)	110.2(2)
		Mean	2.688	Mean	109.4
		Tetrahedron T(11)			
0(1)	1.637(4)	0(1)--0(2)	2.649(5)	0(1)--0(2)	107.9(2)
0(2)	1.639(4)	0(22)	2.654(5)	0(22)	108.2(2)
0(22)	1.638(4)	0(33)	2.715(4)	0(33)	111.7(2)
0(33)	1.643(3)	0(2)--0(22)	2.638(6)	0(2)--0(22)	107.2(2)
Mean	1.639	0(33)	2.712(5)	0(33)	111.4(2)
		0(22)--0(33)	2.691(5)	0(22)--0(33)	110.2(2)
		Mean	2.677	Mean	109.4
Interlayer cation K(1)				T(1) to T(11)	
0(1)x2	2.994(3)	3.286(3)		around 0(1)	139.1(2)
0(2)x2	2.999(4)	3.291(5)		around 0(2)	139.4(2)
0(22)x2	2.978(4)	3.177(4)		around 0(22)	130.5(2)
Mean	2.990 (inner)	3.251 (outer)		Mean	136.3
		Octahedron M(1)			
0(3)x2	2.127(4)			0(3)--0(33)x2	96.8(1)
0(33)x2	2.138(4)			F(1)x2	100.0(1)
F(1)x2	2.130(3)			0(33)--F(1)x2	97.9(1)
Mean	2.132			Mean (unshared)	98.2
0(3)--0(33)x2	3.189(4)			0(3)--0(3)	77.3(2)
F(1)x2	3.261(4)			F(1)x2	88.3(1)
0(33)--F(1)x2	3.219(4)			0(33)--0(33)	89.6(2)
Mean (unshared)	3.223			F(1)x2	74.4(1)
				Mean (shared)	82.1
0(3)--0(3)	2.656(6)				
F(1)x2	2.967(4)				
0(33)--0(33)	3.013(6)				
F(1)x2	2.579(4)				
Mean (shared)	2.794				
		Octahedron M(2)			
0(3)x2	1.889(4)			0(3)--0(33)x2	93.5(1)
0(33)x2	1.895(3)			F(1)x2	92.6(1)
F(1)x2	1.862(3)			0(33)--F(1)x2	91.1(1)
Mean	1.882			Mean (unshared)	92.4
0(3)--0(33)x2	2.755(4)			0(3)--0(3)	89.4(2)
F(1)x2	2.712(3)			0(33)x2	88.6(1)
0(33)--F(1)x2	2.681(4)			0(33)--F(1)x2	86.7(1)
Mean (unshared)	2.716			F(1)--F(1)	85.4(2)
				Mean (shared)	87.6
0(3)--0(3)	2.656(6)				
0(33)x2	2.643(4)				
0(33)--F(1)x2	2.579(4)				
F(1)--F(1)	2.524(5)				
Mean (shared)	2.604				
		Octahedron M(3)			
0(3)x2	2.109(3)			0(3)--0(33)x2	98.6(1)
0(33)x2	2.125(4)			F(1)x2	96.7(1)
F(1)x2	2.159(3)			0(33)--F(1)x2	99.3(1)
Mean	2.131			Mean (unshared)	98.2
0(3)--0(33)x2	3.209(4)			0(3)--0(33)x2	77.3(1)
F(1)x2	3.189(4)			F(1)x2	88.1(1)
0(33)--F(1)x2	3.265(4)			0(33)--0(33)	90.3(2)
Mean (unshared)	3.221			F(1)--F(1)	71.5(1)
				Mean (shared)	82.1
0(3)--0(33)x2	2.643(4)				
F(1)x2	2.967(4)				
0(33)--0(33)	3.013(6)				
F(1)--F(1)	2.524(5)				
Mean (shared)	2.793				

specimens as evidence for ordering, and also noted that the natural specimens were more F-rich than the synthetic specimens, which were grown in equilibrium with a buffer of low fluorine fugacity. The difference of 0.1 A noted in the $d(001)$ values by Rieder probably is due primarily to the presence of fluorine. Calculation of the octahedral sheet thickness in the present study by considering the apical oxygens separately from the (F,OH) atom does result in a difference of 0.1 A. In addition, Yoder and Eugster (1954) showed a decrease in basal spacing of 0.18 A for fluorophlogopite relative to hydroxyphlogopite, where octahedral ordering cannot be a factor. It should be noted also that the clintonite-1*M* (xanthophyllite), the model for the Rieder ordering pattern, actually has an octahedral sheet not appreciably different in thickness (2.148 A) than for disordered F-poor trioctahedral micas (range 2.09–2.22 A).

We suggest that the ordering pattern observed in this study, namely with the small cation in either $M(2)$ or $M(3)$, should be found in all F-rich zinnwaldites and lepidolites. Some evidence for this view can be found in the anomalously high B values for the (F, OH) atom in micas that show the "normal" ordering pattern, with $M(1)$ larger than the average $M(2,3)$ atom, but that have not been refined in subgroup symmetry, namely $B = 2.78$ A^2 in fluor-polylithionite-1*M* (Takeda and Burnham, 1969), $B = 2.92$ and 1.77 A^2 in lepidolite-2M_2 (Takeda *et al.*, 1971; Sartori *et al.*, 1973), and $B = 2.32$ A^2 in lepidolite-1*M* (Sartori, 1976). Additional evidence comes from the cell dimensions of zinnwaldites. Bailey (1975) has shown that the "normal" ordering pattern necessarily gives rise to an intralayer shift larger than the ideal value of $-a/3$ and, unless compensated by an offset of adjacent layers, to an observed β angle for 1*M* micas larger than ideal. It is possible to obtain values of $c\sin\beta$, a, and β for 11 zinnwaldites from graphs presented by Rieder (1968, 1970*b*) and Rieder *et al.* (1971). In all cases the "normal" ordering pattern is predicted, including specimen # 40 whose structure is presented here ($\beta_{obs} = 100.83°$, $\beta_{ideal} = 100.07°$). For three synthetic annites the observed and ideal β angles are approximately equal, as should be true where the octahedra are of similar sizes.

Structural distortions

Important structural features of zinnwaldite-1*M* are summarized in Table 5. Tetrahedra $T(1)$ and $T(11)$ are similar in shape, only slightly elongate, and rotated by 5.8°. The small octahedron $M(2)$ containing Al is nearly regular in shape, but $M(1)$ and $M(3)$ are considerably flattened and distorted (Fig. 1). The individual ψ values of 60.8° (ideal = 54.73°) for $M(1)$ and $M(3)$ are among the largest recorded for micas to date, and are a measure of the amount of flattening required to fit these large Fe,Li-rich octahedra onto

Table 5. Important structural features of zinnwaldite

Parameter	Value
${}^{a}\alpha_{tet}$(°)	5.8
${}^{b}\tau_{tet}$(°)	T(1): 111.0 T(11): 111.1
${}^{e}\beta_{ideal}$(°)	100.07
${}^{c,d}\psi_{oct}$(°)	M(1), M(3): 60.8 M(2): 56.5 Mean: 59.5
^{d}Sheet thickness (Å)	
tetrahedral	2.252
octahedral	2.078
Interlayer separation (Å)	3.333
Basal oxygen Δz_{ave} (Å)	0.124
Intralayer shift	$-0.354a_1$
Layer offset	$-0.004a_1$
Resultant shift	$-0.358a_1$

[a] *Tetrahedral rotation is calculated from* $\alpha = 1/2|120° -$ *mean* O_b-O_b-O_b *angle* $|$.

[b] *The tetrahedral angle is defined as* $\tau = O_{apical}$--T--O_{basal}. *The ideal value is 109.47°.*

[c] *The mean octahedral angle, ideally 54.73°, is calculated from* $\cos\psi$ = *oct. thickness/2*$(\overline{M\text{--}O,F,OH})$.

[d] *Includes the position of F(1) in the calculation.*

[e] $\beta_{ideal} = 180° - \cos^{-1}(\underline{a}/3\underline{c})$.

the adjacent smaller and thinner octahedron (ψ = 56.5°) around the Al in *M*(2). The sheet thicknesses are similar to those found in other F-rich trioctahedral micas.

Apparent thermal vibrations

Tables 6 and 7 list the orientations of the thermal ellipsoids and the calculated bond lengths after correction for thermal effects. The apparent thermal motions of zinnwaldite resemble those of phlogopite (and annite) in some aspects and are unique in others. Like phlogopite, the apparent thermal motions are large in both magnitude and anisotropy. Hazen and Burnham (1973) suggest that such apparent thermal motions are due, in part, to local variations in atomic positions. Also like phlogopite, equivalent isotropic temperature factors of the apical oxygens [O(3) and O(33)] are considerably smaller in magnitude than those of the basal oxygens. These differences in thermal magnitudes may be related to the differences in bond lengths between tetrahedral Al and Si and to lack of appreciable tetrahedral order. The basal oxygens are coordinated to two tetrahedra and are, therefore, more affected by the different Si—O and Al^{IV}—O bond lengths than are the apical oxygens.

In phlogopite most of the atoms are elongate along Z^*. In zinnwaldite the elongation is along Z^* and Z. However, some atoms also appear to be elongate along the bonds to them. Most significantly, the (F,OH) atom is elongate along the bonds to both *M*(1) and *M*(3), and this suggests a small amount of positional disorder for (F,OH). NMR studies of phlogopites with varying amounts of F and OH indicate (1) a tendency for F—F pairing along the same octahedral edge rather than a random distribution, and (2) preferential location of Fe^{2+} in sites close to OH groups (Sanz and Stone, 1977.) This is in accord also with the known preference of Al for F rather than for OH, as summarized by Kampf (1977). It is interesting to note in the Sadisdorf zinnwaldite specimen that OH makes up 39 percent of the F,OH total and that Fe^{2+} also makes up 39 percent of the total occupancy of *M*(1) + *M*(3). This may indicate a local clustering or domain structure, in which 39 percent of the volume of the crystal consists of OH—OH pairs located closer to Fe^{2+} in *M*(1) and *M*(3) than to Al in *M*(2), and 61 percent consists of F—F pairs located

Table 6. Orientations of thermal ellipsoids relative to crystal axes

Atom	Axis	rms (Å) displacement	Angle (°) with respect to X	Y	Z
K(1)	r_1	0.143(2)	90	0	90
	r_2	0.156(2)	150(6)	90	109(6)
	r_3	0.168(2)	120(6)	90	19(6)
M(1)	r_1	0.062(4)	90	0	90
	r_2	0.091(2)	163(5)	90	62(5)
	r_3	0.110(2)	73(5)	90	28(5)
M(2)	r_1	0.078(4)	90	0	90
	r_2	0.082(3)	178(13)	90	77(13)
	r_3	0.093(4)	88(13)	90	13(13)
M(3)	r_1	0.071(5)	90	0	90
	r_2	0.080(3)	156(5)	90	103(5)
	r_3	0.110(3)	114(5)	90	13(5)
T(1)	r_1	0.063(4)	102(5)	14(4)	80(4)
	r_2	0.084(3)	145(11)	95(6)	113(12)
	r_3	0.094(3)	122(11)	103(4)	25(11)
T(11)	r_1	0.061(4)	100(8)	10(8)	88(3)
	r_2	0.078(3)	169(7)	100(8)	84(4)
	r_3	0.104(3)	94(4)	91(3)	7(4)
O(1)	r_1	0.095(5)	89(4)	7(13)	83(12)
	r_2	0.121(4)	99(3)	83(13)	159(5)
	r_3	0.171(4)	9(3)	89(4)	110(3)
O(2)	r_1	0.106(6)	145(7)	118(9)	62(21)
	r_2	0.117(6)	99(19)	111(11)	151(21)
	r_3	0.167(5)	123(4)	36(4)	97(5)
O(22)	r_1	0.102(6)	132(7)	53(4)	106(10)
	r_2	0.127(6)	61(9)	94(9)	161(10)
	r_3	0.157(5)	56(5)	37(4)	82(7)
O(3)	r_1	0.076(6)	130(8)	41(8)	76(12)
	r_2	0.098(5)	96(22)	86(18)	162(18)
	r_3	0.106(5)	40(9)	50(8)	100(25)
O(33)	r_1	0.087(5)	26(18)	106(26)	81(11)
	r_2	0.097(5)	105(26)	164(27)	93(27)
	r_3	0.107(5)	110(12)	90(26)	9(12)
F(1)	r_1	0.096(5)	72(7)	25(5)	110(5)
	r_2	0.121(4)	145(12)	84(9)	113(13)
	r_3	0.134(4)	118(13)	66(5)	31(10)

Table 7. Bond lengths corrected for thermal motion

Bond	Distance (Å) Correlation high	none	Bond	Distance (Å) Correlation high	none
M(1) octahedron					
0(3)x2	2.128(4)	2.136(4)			
0(33)x2	2.140(4)	2.148(4)			
F(1)x2	2.142(3)	2.149(3)			
Mean	2.137	2.144			
0(3)-0(3)	2.660(6)	2.667(6)	0(3)-0(33)x2	3.189(4)	3.195(4)
F(1)x2	2.971(4)	2.977(4)	F(1)x2	3.275(4)	3.279(4)
0(33)-0(33)	3.019(6)	3.025(6)	0(33)-F(1)x2	3.220(4)	3.226(4)
F(1)x2	2.583(4)	2.590(4)			
Mean (shared)	2.798	2.804	Mean (unshared)	3.228	3.233
M(2) octahedron					
0(3)x2	1.890(4)	1.898(4)			
0(33)x2	1.896(3)	1.904(3)			
F(1)x2	1.866(3)	1.874(3)			
Mean	1.884	1.892			
0(3)-0(3)	2.660(6)	2.667(6)	0(3)-0(33)x2	2.755(4)	2.762(4)
0(33)x2	2.645(4)	2.652(4)	F(1)x2	2.714(3)	2.721(3)
0(33)-F(1)x2	2.583(4)	2.590(4)	0(33)-F(1)x2	2.683(4)	2.690(4)
F(1)-F(1)	2.527(5)	2.537(5)			
Mean (shared)	2.607	2.615	Mean (unshared)	2.717	2.724
M(3) octahedron					
0(3)x2	2.109(3)	2.117(3)			
0(33)x2	2.126(4)	2.133(4)			
F(1)x2	2.161(3)	2.169(3)			
Mean	2.132	2.140			
0(3)-0(33)x2	2.645(4)	2.652(4)	0(3)-0(33)x2	3.210(4)	3.215(4)
F(1)x2	2.971(4)	2.977(4)	F(1)x2	3.189(4)	3.196(4)
0(33)-0(33)	3.019(6)	3.025(6)	0(33)-F(1)x2	3.267(4)	3.273(4)
F(1)-F(1)	2.527(5)	2.537(5)			
Mean (shared)	2.796	2.803	Mean (unshared)	3.222	3.228
T(1) tetrahedron					
0(1)	1.655(4)	1.664(4)	0(1)-0(2)	2.660(5)	2.674(5)
0(2)	1.649(4)	1.656(4)	0(22)	2.655(5)	2.670(5)
0(22)	1.654(4)	1.663(4)	0(3)	2.717(4)	2.732(4)
0(3)	1.654(4)	1.661(4)	0(2)-0(22)	2.664(6)	2.677(6)
Mean	1.653	1.661	0-(3)	2.723(5)	2.738(5)
			0(22)-0(3)	2.702(5)	2.716(5)
			Mean	2.687	2.701
T(11) tetrahedron					
0(1)	1.645(4)	1.655(4)	0(1)-0(2)	2.650(5)	2.666(5)
0(2)	1.647(4)	1.656(4)	0(22)	2.659(5)	2.673(5)
0(22)	1.645(4)	1.654(4)	0(33)	2.711(4)	2.726(4)
0(33)	1.645(3)	1.651(3)	0(2)-0(22)	2.637(6)	2.652(6)
Mean	1.646	1.654	0(33)	2.708(5)	2.722(5)
			0(22)-0(33)	2.688(5)	2.701(5)
			Mean	2.676	2.690
Interlayer cation K(1)					
0(1)x2	2.991(3)	3.007(3)			
0(2)x2	2.997(4)	3.013(4)			
0(22)x2	2.975(4)	2.991(4)			
Mean (inner)	2.988	3.004			
0(1)x2	3.294(3)	3.307(3)			
0(2)x2	3.292(5)	3.307(5)			
0(22)x2	3.177(4)	3.193(4)			
Mean (outer)	3.254	3.269			

closer to Al in $M(2)$ than to Li and the remaining cations in $M(1)$ and $M(3)$. Under this interpretation the bulk of the thermal ellipsoid of (F,OH) is determined by the positions of the F (61 percent), and the elongation toward $M(1)$ and $M(3)$ is produced by the closer approach of the OH (39 percent) to the Fe in those sites. In addition to the elongation of (F,OH) along the $M(1)$ and $M(3)$ bonds, the $M(1)$ site is observed to be elongate along the $M(1)$—(F,OH) bond.

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