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A NEUTRON-DIFFRACTION STUDY OF THE FERRIC TOURMALINE, BUERGERITE[1]

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ABSTRACT

The structural parameters of buergerite (ideally $NaFe_3B_3Al_6Si_6O_{30}F$) have been refined using three-dimensional, single-crystal neutron diffraction data. The occupancy factors in the cation sites have also been refined, and, in agreement with the X-ray results, a substitution of Fe into the 18*c* Al point position of space group *R3m* is found.

A difference synthesis resulted in the location of a hydrogen atom in the structure—corresponding to the replacement of O by OH in one site of the FeO_6 octahedron about 8 percent of the time.

Because of the differences in scattering amplitudes, some of the bond distances have been determined to slightly higher precision than in the X-ray determination. The final R (F^2) factor for 391 independent reflections is 0.034. The maximum error in the final difference synthesis is 0.4 fm $Å^{-3}$—about 1 percent of the maximum peak height in the observed scattering density map. The position and thermal parameters agree extraordinarily well with those of the X-ray study, and confirm the results of that work in detail; the precision of the atomic position determinations is about 0.003 Å in both studies.

A comparison of neutron powder diffraction patterns at 300°K and at 4.2°K provides no evidence for magnetic ordering or other structural change between these temperatures.

INTRODUCTION

Buergerite, a ferric tourmaline with the idealized formula $NaFe_3B_3Si_6Al_6O_{30}F$, has been described by Mason, Donnay, and Hardie (1964) and by Donnay, Ingamells, and Mason (1966). In a recent X-ray diffraction study Barton (1969) found the crystal structure of buergerite to be very similar to the dravite structure of Buerger, Burnham, and Peacor (1962). An important result of the X-ray study is that some iron replaces aluminum in the 18*c* position of space group *R3m*, a substitution not demanded by the chemical analysis. The ratios of atomic scattering amplitudes for neutrons and X-rays differ; therefore a neutron diffraction study should provide independent evidence of cation substitution. Furthermore, neutron diffraction data are senstitive to the ordering of unpaired electrons, and a report of the antiferromagnetic behavior of buergerite (Tsang, Thorpe, Senftle, and Donnay, 1970) gave further stimulus to the study reported in this paper.

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CRYSTAL DATA

The cell constants, density, and space group were taken as those found in the X-ray study: $a=15.869$ Å, $c=7.188$ Å, $\rho_x=3.29$ g cm^{-3}, $R3m$.

EXPERIMENTAL

The crystalline material used in this investigation was kindly supplied by Dr. John S. White of the U. S. National Museum (specimen R-12631), and was from the same locality as the crystals studied in the investigations referenced above. The final formula adopted by Barton on the basis of the chemical analysis and the x-ray structure determination is

$$Na_{2.49}K_{0.05}Ca_{0.39}\square_{0.07})(M_{6.30}Al_{2.65}\square_{0.05})B_{9.00}(Al_{16.32}M_{1.57}\square_{0.11}) \cdot (Si_{17.20}B_{0.80})(O_{88.53}OH_{1.39}F_{0.08})F_{3.00}.$$

with $M=Fe_{0.951}+Ti_{0.028}+Mg_{0.013}+Mn_{0.008}$. This overall chemical composition was assumed in the present study, and the distribution of the cations was essentially confirmed.

A doubly terminated prismatic crystal was chosen for data collection. The distance between the two monohedra and between the three pairs of opposite prism faces ($10\bar{1}0$, $01\bar{1}0$, $11\bar{2}0$) were each equal to 1.90 mm. The crystal volume was 6.25 mm^3. The crystal was mounted with the [110] axis parallel to the ϕ axis of a four-circle goniometer at the Brookhaven National Laboratory High Flux Beam Reactor. A monochromatic beam of neutrons with wavelength 1.047 Å was obtained by reflection from the (111) face of a single crystal of copper; at this wave-length, the amount of second order contamination in the beam is negligible.

Integrated intensities were obtained for reflections with $(\sin\theta)/\lambda<0.65$ by a θ–2θ step scan-method, with steps taken every 0.1 degree in 2θ. The length of the scan was a variable function of scattering angle, chosen to obtain several background points at each end of the scan. The data were reduced to squared structure amplitudes by background correction, application of the Lorentz factor $\sin 2\theta$, and correction for absorption ($\mu=4.36$ cm^{-1}). The transmission factors varied from 0.46 to 0.52. Most reflections were observed twice; 822 separate (hkl) values were obtained from 1644 measurements. The agreement factors R and R_ω for the 585 multiply-observed reflections were 0.023 and 0.025.[1] Only seventeen of these reflections deviated by more than 4σ from the weighted mean.

The intensities for the 822 (hkl) values were now averaged over sets of symmetry-equivalent reflections to obtain 397 independent reflections. The values of R and R_ω for this averaging were 0.024 and 0.025; no departure from Laue symmetry $\bar{3}m$ was suggested. For the subsequent analysis, each reflection was assigned an estimated standard deviation which was the highest of the following three values: (1) the counting statistical error, (2) the standard deviation of the mean as estimated from the agreement between equivalent reflections, (3) five percent of F^2.

STRUCTURE REFINEMENT

Initial least squares refinement of all position parameters, anisotropic thermal parameters, an isotropic extinction parameter (Zachariasen, 1967), a scale factor, and atomic scattering lengths for all positions ex-

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[1] $$R = \sum_{hkl,j} \left| F_j^2(hkl) - F_\mu^2(hkl) \right| \Big/ \sum_{hkl,j} F_\mu^2(hkl)$$

$$R_\omega = \left[\sum_{hkl,j} \omega_j \left| F_j^2(hkl) - F_\mu^2(hkl) \right|^2 \Big/ \sum_{hkl,j} F_\mu^4(hkl) \right]^{1/2}$$

with the weights $\omega_j = 1/\sigma_j^2$ being determined by Poisson counting statistics.

TABLE 1. NEUTRON SCATTERING LENGTHS IN 10^{-12} CM FOR THE ELEMENTS IN BUERGERITE

Those values with standard deviations in parentheses were refined in this study, and mean values are based on the chemical composition given by Barton.

Atom	Atomic Number	b
Na	11	0.351
K	19	0.37
Ca	20	0.49
μ(Na site)	—	0.361
Fe	26	0.95
Ti	22	−0.34
Mg	12	0.52
Mn	25	−0.36
$\mu(M)$	—	0.898
Al	13	0.35
B	5	0.540 (9)
O	8	0.577
F	9	0.55
H	1	−0.378
Fe site	—	0.763 (11)
Al site	—	0.385 (7)

cept the 18*c* Al position (which was normalized to agree with Barton's results) indicated that the chemical composition given by Barton and the neutron scattering lengths given in Table 1 are indeed satisfactory. In subsequent refinements, most scattering lengths were fixed at their theoretical values. Exceptions were made for the 18*c* Al position and the 9*b* Fe position; the scattering lengths at these positions were varied to obtain an independent estimate of the (Al, Fe) replacement found by Barton.[1] The boron scattering length was also refined, inasmuch as it is not as well characterized by previous crystallographic studies. The O(1) site was assumed to be entirely F; the scattering lengths for F and O are nearly equal, and a moderate substitution of O for F would not affect the results.

Refinement of position, thermal, scale, and extinction parameters along with the three scattering lengths reduced the value of R and R_ω (both based on F^2) to 0.036 and 0.061. The standard deviation of an observation of unit weight (S) was 1.276. Observed and difference scattering density syntheses were calculated at this stage. Peak heights in the observed map ranged from 44.96 fm·Å^{-3} for Fe to 21.25 fm·Å^{-3} for

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[1] The restraint on the 18*c* Al scattering length in the previous refinement does not affect the results of the final refinement; effectively, in the final refinements, normalization was made to the scattering factor for oxygen, which is well known.

Na (one Fermi or femtometer (fm) $= 10^{-15}$ m). Figure 1 shows a section of this map in a plane near the plane of the BO_3 triangle. The maximum peak heights in the difference map were 0.42 fm·Å^{-3}, and there were many peaks nearly this high scattered uniformly throughout the cell. Thus the noise level may be taken as about 0.4 fm·Å^{-3}. Negative peaks (see Figure 2), which will correspond to hydrogen atoms, were found above this noise level at only two chemically reasonable positions (about 1 Å from oxygen sites) and not too close to other atoms. The largest peak occurred at (-0.13, $+0.13$, 0.39) with a density of -0.99 fm·Å^{-3}; this is approximately 1 Å from O(3) along the O(3)$-$O(5) line. A second peak with a density of -0.59 fm·Å^{-3} was found at (0.00, 0.00, -0.12). This is about 1 Å from the O(1)$\equiv$F site. A peak with a density of -0.61 fm·Å^{-3} was found about 1 Å from B and 1.8 Å from O_8; a peak with density -0.55 fm·Å^{-3} was found at about 1 Å from O(5) but at 1.8 Å from Si; three other peaks with densities between 0.40 and 0.48 fm·Å^{-3} were either too close to Fe or a long distance from any atom; all these peaks were judged to be either noise or diffraction ripple from the heavy atoms. Least squares refinement of the positions and occupancy factors for the two reasonable hydrogen atom sites led to occupancies of 0.083(11) for H(03) in a *9b* position and 0.006(20) for H(F) in a *3a* position. Thus the refinement would seem to indicate essentially no hydrogen in the latter position. After the final cycles of least squares refinement including only the H(03) hydrogen atom, a final difference synthesis now had its largest peak at the position (0, 0, -0.14) with a density of -0.5 fm·Å^{-3}, but there was a steady gradation of noise peaks falling off from this level. Although charge-balance considerations (Donnay, 1970) suggest significant hydrogen occupancies in both positions, the ionic disorder in both the Na^+ and F^- positions on the three-fold axis (as evidenced by the high thermal parameters) may also smear out the hydrogen atom so that it is not quite distinguishable from the noise in the difference synthesis, and the occupancy factor for this atom becomes poorly determined. The amount of H in the H(03) site corresponds to 0.75(10) H atoms per unit cell. The chemical analysis suggests a total hydrogen content of 1.4; thus at least half of the hydrogen in the cell is in the form of OH at the O(3) position, and is located such that a weak hydrogen bond occurs between O_3 and O_5. The geometrical parameters of this hydrogen bond are O_3-H 0.94(5), $H\ldots O_5$ 2.46(5), $\angle O_3-H\ldots O_5$ 155°(2).[1]

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[1] Hamilton and Ibers (1968) have given the geometrical criterion for a hydrogen bond as the existence of a heavy atom-hydrogen atom contact at least 0.2 A less than the sum of the van der Walls radii. (The last sentence in section 1.7 of this reference is unfortunately garbled.) Thus this would not be a hydrogen bond by the Hamilton-Ibers criterion. This is in agreement with the charge balance considerations of Donnay (1970).

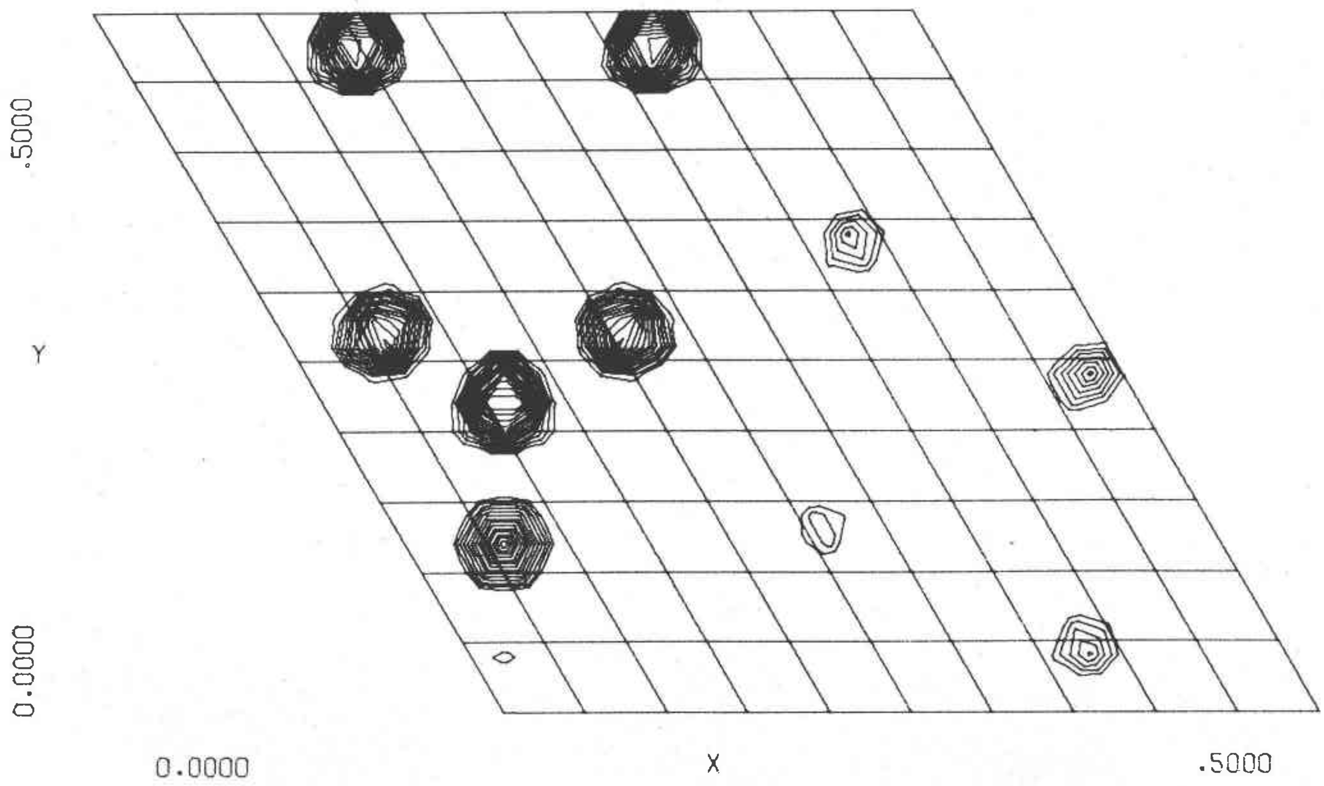

FIG. 1. Section ($z=0.4600$) of the three-dimensional neutron scattering density map for buergerite. This section shows the BO_3 triangle clearly, as well as two O(6) atoms nearly in the plane. The smaller peaks are O(3), O(4), and two O(7) atoms which do not lie in the plane of the section. The contour interval is 0.225 fm·Å^{-3}, and the minimum contour is at 0.45 fm·Å^{-3}.

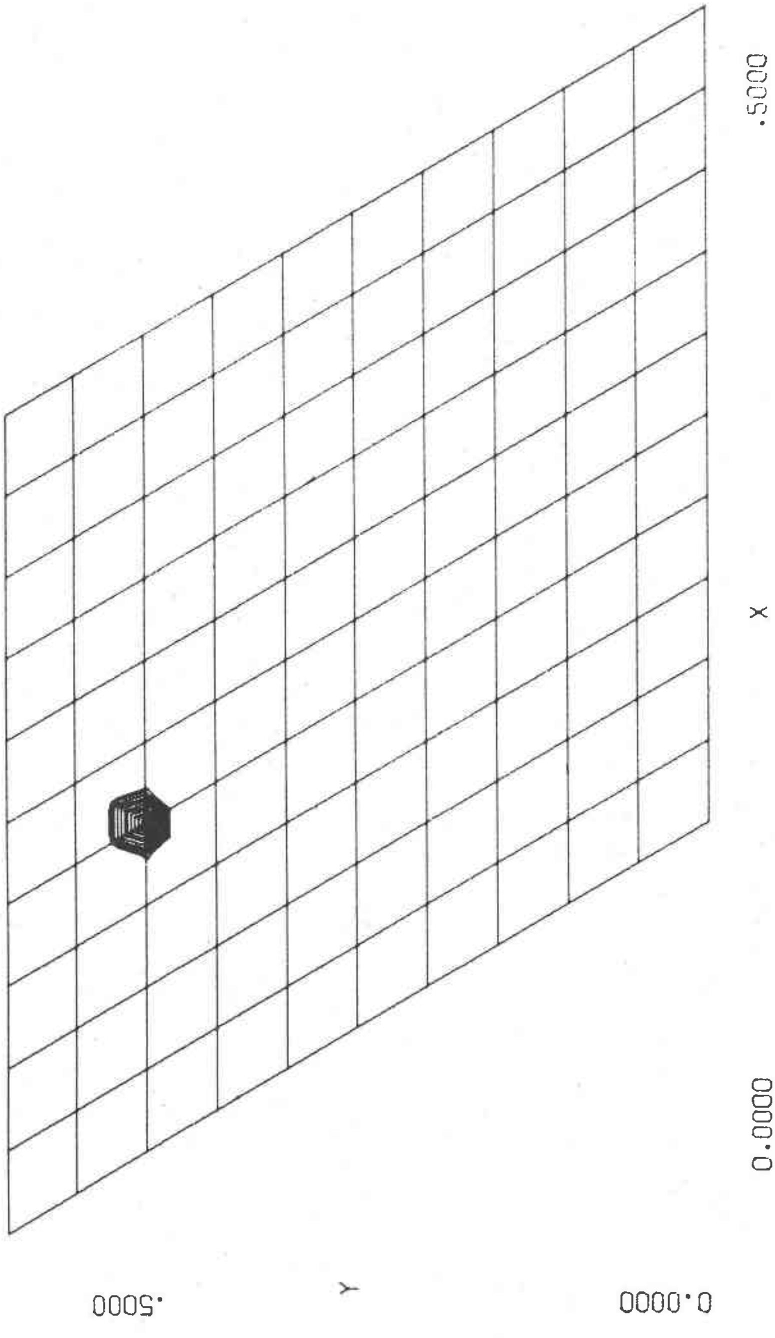

FIG. 2. Neutron scattering density map ($z = 0.0600$) in the neighborhood of the hydrogen atom attached to O(3). The minimum contour is at -0.41 fm·Å^{-3}, the interval is -0.045 fm·Å^{-3}, and the hydrogen atom peak has a density of -0.91 fm·Å^{-3}.

A final cycle of least squares refinement, varying all parameters for the heavy atoms, but keeping an isotropic thermal parameter fixed at 2.4 A^2 for H(O3), resulted in the structural parameters of Tables 2 and 3. The observed and calculated values of F^2 are presented in Table 4.

TABLE 2. POSITIONAL PARAMETERS IN BUERGERITE

Neutron parameters on first line, x-ray on second. Standard deviations in parentheses.

Atom	x	y	z
Na (3*a*)	0	0	0.21186 (139)
	0	0	0.21338 (41)
B (9*b*)	0.11001 (9)	$-x$	0.45172 (50)
	0.10992 (25)	$-x$	0.45182 (46)
Fe (9*b*)	−0.06614 (8)	$-x$	0.62217 (48)
	−0.06660 (4)	$-x$	0.62072 (10)
Si (18*c*)	0.19171 (17)	0.19087 (17)	0
	0.19156 (4)	0.19065 (4)	0
Al (18*c*)	0.29925 (19)	0.25919 (18)	0.60450 (54)
	0.29880 (4)	0.25887 (4)	0.60437 (10)
O(1)=F (3*a*)	0	0	0.76850 (74)
	0	0	0.76698 (51)
O(2) (9*b*)	0.06042 (9)	$-x$	0.48532 (54)
	0.06056 (15)	$-x$	0.48607 (29)
O(3) (9*b*)	−0.13205 (10)	$-x$	0.52026 (48)
	−0.13225 (17)	$-x$	0.52094 (30)
O(4) (9*b*)	0.09463 (9)	$-x$	0.07612 (50)
	0.09478 (15)	$-x$	0.07532 (28)
O(5) (9*b*)	−0.09117 (11)	$-x$	0.08362 (52)
	−0.09129 (16)	$-x$	0.08388 (28)
O(6) (18*c*)	0.19320 (13)	0.18712 (12)	0.77538 (41)
	0.19314 (11)	0.18680 (11)	0.77481 (18)
O(7) (18*c*)	0.28708 (12)	0.28592 (11)	0.07513 (44)
	0.28670 (10)	0.28580 (10)	0.07445 (18)
O(8) (18*c*)	0.20925 (13)	0.26971 (12)	0.43868 (43)
	0.20894 (10)	0.26941 (10)	0.43778 (20)
H (9*b*)	−0.1313 (19)	$-x$	0.3889 (72)

TABLE 3. THERMAL PARAMETERS[a] FOR BUERGERITE
Neutrons on first line, X-rays on second, standard deviations in parentheses

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	325 (29)	β_{11}	720 (163)	$\frac{1}{2}\beta_{11}$	0	0
	302 (14)	β_{11}	1172 (58)	$\frac{1}{2}\beta_{11}$	0	0
B	59 (12)	β_{11}	340 (50)	33 (11)	18 (10)	$-\beta_{13}$
	62 (16)	β_{11}	263 (40)	38 (10)	5 (17)	$-\beta_{13}$
Fe	103 (9)	β_{11}	585 (46)	15 (7)	87 (8)	$-\beta_{13}$
	72 (3)	β_{11}	544 (10)	3 (2)	87 (4)	$-\beta_{13}$
Si	63 (12)	62 (11)	294 (44)	29 (9)	−5 (17)	−34 (17)
	40 (2)	38 (2)	152 (8)	18 (2)	3 (4)	−8 (4)
Al	63 (15)	58 (14)	233 (50)	14 (10)	−7 (20)	41 (19)
	64 (2)	86 (3)	286 (9)	34 (2)	−7 (4)	35 (4)
O(1)=F	192 (15)	β_{11}	359 (85)	$\frac{1}{2}\beta_{11}$	0	0
	378 (24)	β_{11}	328 (66)	$\frac{1}{2}\beta_{11}$	0	0
O(2)	99 (9)	β_{11}	415 (45)	77 (10)	9 (9)	$-\beta_{13}$
	103 (14)	β_{11}	516 (36)	77 (8)	9 (14)	$-\beta_{13}$
O(3)	67 (9)	β_{11}	381 (49)	−4 (10)	−11 (10)	$-\beta_{13}$
	82 (12)	β_{11}	367 (33)	14 (8)	8 (15)	$-\beta_{13}$
O(4)	86 (9)	β_{11}	356 (47)	33 (10)	−20 (10)	$-\beta_{13}$
	93 (13)	β_{11}	330 (33)	33 (8)	−5 (15)	$-\beta_{13}$
O(5)	95 (8)	β_{11}	298 (41)	15 (10)	−3 (9)	$-\beta_{13}$
	95 (13)	β_{11}	330 (32)	24 (8)	−12 (15)	$-\beta_{13}$
O(6)	71 (8)	79 (8)	202 (28)	22 (6)	1 (13)	−6 (12)
	88 (6)	73 (6)	274 (20)	32 (5)	5 (10)	−2 (9)
O(7)	61 (8)	47 (9)	315 (30)	12 (6)	1 (13)	−21 (13)
	81 (6)	69 (6)	237 (20)	28 (5)	−17 (9)	−23 (9)
O(8)	39 (9)	96 (8)	411 (31)	26 (7)	32 (13)	52 (13)
	62 (5)	87 (6)	381 (22)	40 (5)	−1 (9)	23 (9)

[a] Debye-Waller factor is exp $\{-\sum_{i,j} h_i h_j \beta_{ij}\}$

The final values of R and R_ω (based on F^2) are 0.034 and 0.056. The value of S, the standard deviation of an observation of unit weight, is 1.164. The values of σ assigned as discussed above are also tabulated in Table 4.

TABLE 4. OBSERVED AND CALCULATED VALUES OF F^2 FOR BUERGERITE
Also given is the value of $\sigma(F^2_{obs})$ as used in all least squares refinements. Units are 10^{-25} cm² (or 10 f²). [The following reflections which contained obvious gross errors in recording are omitted from the table (h, k, l, FO, SIG, FC): (0, 7, 8, 20, 6, 142), (2, 14, 3, 354, 24, 184), (4, 1, 3, 74, 11, 9), (4, 2, 2, 376, 19, 241), (9, 1, 5, 32, 12, 133), (17, 1, 1, 181, 22, 294).]

L= 0

K	H	FO	SIG	FC
2	2	1744	87	1681
3	0	55	5	47
3	3	657	33	608
4	1	154	8	159
4	4	1292	65	1376
5	2	189	24	176
5	5	5897	295	5825
6	0	26	4	16
6	3	222	11	201
6	6	5486	274	5340
7	1	230	16	230
7	4	994	50	997
7	7	1817	91	1733
8	2	1192	60	1268
8	5	1688	84	1696
8	8	243	16	257
9	0	1224	61	1199
9	3	3221	161	3262
9	6	586	29	580
10	1	4756	238	4852
10	4	191	11	182
10	10	5093	255	5421
11	2	107	9	81
11	5	214	18	196
11	8	755	38	771
12	0	618	59	590
12	3	345	17	335
12	6	627	34	562
13	1	84	13	100
13	4	357	18	382
13	7	802	40	777
15	0	6061	303	6260
15	3	1621	81	1561
16	1	995	50	941

L= 1

K	H	FO	SIG	FC
0	4	229	11	219
0	7	538	27	484
0	10	8227	411	8220
0	13	344	17	352
0	16	1538	96	1425
1	2	366	18	380
1	5	1164	58	1204
1	8	466	23	460
1	11	1591	80	1605
1	14	749	37	720
2	0	314	16	356
2	3	418	21	438
2	6	1192	60	1198
2	9	192	16	156
2	12	1170	58	1261
2	15	452	41	513
3	1	81	7	89
3	4	3068	152	2962
3	7	704	35	711
3	10	1269	63	1287
3	13	291	15	292
4	2	66	5	62
4	5	422	21	439
4	8	815	41	792
4	11	355	18	373
4	14	1544	77	1513
5	0	4711	236	4652
5	3	49	4	33
5	6	4197	210	4162
5	9	652	33	611
5	12	322	24	329
6	1	846	42	836
6	4	515	26	509
6	7	1229	61	1277
6	10	911	46	975
6	13	780	39	754
7	2	2649	132	2615
7	5	1318	66	1280
7	8	302	15	281
7	11	777	39	825
8	0	178	9	190
8	3	65	9	74
8	6	2290	114	2273
8	9	1018	51	1008
8	12	971	49	938
9	1	392	20	400
9	4	704	36	691
9	7	727	36	742
9	10	592	30	510
10	2	810	41	795
10	5	1481	74	1565
10	8	837	42	840
11	0	6347	317	6166
11	3	484	40	516
11	6	1401	70	1341
11	9	323	20	374
12	1	136	13	135
12	4	430	26	418
12	7	669	39	724
13	2	548	27	529
13	5	337	17	318
14	0	226	16	240
14	3	2109	105	2163
15	1	2606	130	2673
15	4	1132	57	1052

L= 2

K	H	FO	SIG	FC
0	2	202	10	217
0	5	850	68	722
0	8	366	18	349
0	11	462	23	461
0	14	369	18	343
1	0	1637	82	1754
1	3	196	10	176
1	6	261	26	228
1	9	671	34	643
1	12	1021	51	1000
1	15	226	21	251
2	1	1851	93	1935
2	7	377	20	403
2	10	603	30	631
2	16	387	94	458
3	2	510	26	540
3	5	324	16	321
3	8	821	41	789
3	11	231	12	237
3	14	1394	70	1406
4	0	893	45	904
4	3	5178	259	5350
4	6	1478	74	1480
4	9	1117	82	1115
4	12	750	37	720
5	1	5519	276	5515
5	4	693	35	693
5	7	690	35	740
5	10	271	14	275
5	13	1346	67	1279
6	2	576	29	571
6	5	114	6	101
6	8	3238	162	3468
6	11	227	19	213
7	0	207	10	219
7	3	41	4	39
7	6	808	57	840
7	9	82	16	135
7	12	416	21	424
8	1	425	21	413
8	4	711	36	720
8	7	293	17	294
9	5	1760	88	1671
9	11	280	21	264
10	0	1073	111	980
10	3	183	10	160
10	6	3834	192	3990
10	9	319	17	298
11	1	225	50	128
11	4	1595	80	1695
11	7	345	17	335
12	2	678	34	689
12	5	242	14	243
12	8	889	44	888
13	0	185	10	180
13	3	535	27	546
13	6	780	39	769
14	1	327	32	320
14	4	2022	101	2014
15	2	219	28	311

L= 3

K	H	FO	SIG	FC
0	0	9995	500	9863
0	3	923	111	846
0	6	1140	57	1131
0	9	1490	74	1435
0	12	1192	60	1116
0	15	851	44	801
1	1	98	10	104
1	7	321	16	325
1	10	6723	336	6628
1	13	325	16	314
1	16	234	17	280
2	2	1146	57	1208
2	5	11	7	13
2	8	418	21	402
2	11	316	16	314
2	14	164	19	199
3	0	2079	104	2039
3	3	847	42	870
3	6	1243	62	1243
3	9	599	37	521
3	12	1028	54	1053
4	1	1328	66	1335
4	4	421	21	394
4	7	63	6	62
4	10	75	7	77
4	13	394	27	370
5	2	73	5	67
5	5	654	33	659
6	0	4035	200	4005
6	3	722	36	716
6	6	1338	67	1437
6	9	2734	137	2670
6	12	1748	87	1759
7	1	772	39	795
7	7	2761	138	2827
7	10	815	41	843
8	2	373	25	377
8	5	609	30	617
8	8	331	17	340
8	11	451	23	455
9	0	521	151	352
9	3	2284	114	2186
9	6	2306	115	2167
9	9	1335	67	1419
10	1	1172	59	1117
10	4	1347	67	1385
10	7	1386	69	1458
11	2	294	15	290
11	5	1741	87	1812
11	8	172	19	205
12	3	400	20	427
12	6	931	47	877
13	1	694	35	661
13	4	995	50	932
15	0	1207	60	1126
15	3	1518	76	1575

L= 4

K	H	FO	SIG	FC
0	1	1322	66	1383
0	4	1881	94	1856
0	7	2224	111	2141
0	10	2084	104	1875
0	13	1248	62	1189
0	16	2505	125	2581
1	2	147	7	148
1	5	3169	158	3202
1	8	1276	64	1290
1	11	73	12	69
1	14	591	88	460
2	0	1119	56	1211
2	3	360	18	364
2	6	1048	52	1100
2	9	258	18	249
2	12	398	20	416
2	15	944	47	976
3	1	336	17	362
3	4	4257	213	4323
3	7	303	18	337
4	2	755	38	723
4	5	1461	73	1457
4	8	440	25	459
4	11	892	45	858
5	0	5485	274	5490
5	3	1315	66	1337
5	6	2285	114	2313
5	9	924	46	901
5	12	483	60	423
6	1	29	5	17
6	4	226	11	240
6	7	982	49	973
6	10	2675	134	2762
7	2	1494	75	1570
7	5	509	25	510
7	8	2358	118	2375
7	11	511	26	574
8	0	546	27	547
8	6	2638	132	2781
8	9	679	34	664
9	1	945	47	913
9	4	565	67	574
9	7	320	16	309
10	2	307	15	317
10	5	1696	85	1744
10	8	290	21	275
11	0	9613	481	8824
11	6	1162	58	1077
12	1	219	17	208
12	4	2122	106	1984
13	2	1546	77	1481
13	5	972	49	932
14	0	586	29	589
14	3	709	35	704
15	1	1691	91	1653

L= 5

K	H	FO	SIG	FC
0	2	909	45	919
0	5	13866	693	13656
0	8	806	40	783
0	11	1626	81	1572
0	14	948	47	956
1	0	1220	61	1300
1	3	28	6	17
1	6	872	44	905
1	12	823	45	858
2	1	239	12	246
2	4	144	7	149
3	2	563	83	514
3	5	311	38	373
3	11	653	33	629
4	0	2083	104	2063
4	3	3716	186	3797
4	6	223	12	237
4	9	1240	62	1138
4	12	1826	91	1839
5	1	1038	52	1100
5	4	359	58	305
5	7	704	35	708
5	10	6240	312	6295
6	2	387	22	381
6	5	3150	157	3173
6	8	2291	115	2197
6	11	2062	103	1934
7	0	135	12	143
7	3	162	23	172
7	6	2175	109	2195
7	9	593	30	643
8	1	73	34	65
8	4	729	36	749
8	7	832	42	809
9	2	1134	57	1092
9	5	597	30	618
9	8	172	18	214
10	0	1194	60	1127
10	3	2127	106	2126
10	6	1997	100	1902
11	1	1035	52	971
11	4	262	19	231
12	2	820	109	646
13	0	830	41	710
14	1	398	20	382

L= 6

K	H	FO	SIG	FC
0	0	11562	578	11092
0	3	86	9	97
0	6	578	29	586
0	9	275	14	278
0	12	1370	69	1287
1	1	386	19	394
1	4	433	22	400
1	7	187	17	183
1	10	1452	73	1456
2	2	694	50	729
2	5	274	14	270
3	0	1591	80	1661
3	3	1209	60	1234
3	6	228	29	207
3	9	1329	66	1313
4	1	1122	56	1051
4	4	1320	66	1308
4	7	149	13	160
4	10	856	40	766
5	2	453	23	468
5	5	2593	130	2568
6	0	475	24	489
6	3	120	8	126
6	6	3237	162	3029
7	1	263	13	272
7	7	2760	138	2727
8	2	62	19	66
8	5	337	48	220
9	0	366	33	390
9	3	2359	103	2368
10	1	4196	210	4237
11	2	438	33	420

L= 7

K	H	FO	SIG	FC
0	1	2878	144	3015
0	4	304	21	350
0	7	721	36	719
0	10	2642	132	2527
1	2	277	14	274
1	5	623	31	609
1	8	759	38	792
2	0	347	17	338
2	3	380	38	371
2	6	215	11	215
3	1	251	13	240
3	4	2198	110	2208
3	7	1232	62	1165
3	10	770	38	766
4	5	522	26	539
5	0	188	14	180
5	6	2648	132	2614
6	1	99	11	119
6	4	1114	56	1127
6	7	622	42	620
7	2	1330	67	1371
7	5	493	25	510
8	0	258	17	253
8	3	342	47	347
9	4	473	27	483
10	2	64	15	99
11	0	704	35	699

L= 8

K	H	FO	SIG	FC
0	2	1568	78	1554
0	5	1791	90	1823
0	8	489	29	505
1	6	181	24	269
2	1	245	14	267
3	2	326	16	312
3	5	852	65	857
4	3	5499	275	5442
4	6	1468	73	1424
5	1	2082	104	2080
5	4	2410	120	2341
6	2	673	34	634

L= 9

K	H	FO	SIG	FC
0	0	4599	230	4415
0	3	1939	97	1931
1	4	1185	59	1106
3	0	525	27	539
4	1	3037	152	3094

COMPARISON OF X-RAY AND NEUTRON RESULTS

The agreement between the X-ray and neutron parameters is quite good. The precision of both determinations is about 0.002–0.004 Å for most interatomic distances. The most significant position parameter difference between the two studies is in the x parameter of the Fe position $P_n - P_x = 0.00046(9)$, but this difference is less than 0.01 Å. The agreement between the thermal parameters is also satisfactory, although as is usual with neutron/X-ray comparisons the discrepancy is greater for the thermal parameters (Hamilton, 1969). The largest deviation is for

TABLE 5. SOME BOND-LENGTH COMPARISONS BETWEEN THE NEUTRON AND X-RAY STUDIES OF BUERGERITE

		Neutrons	X-rays
Si_6O_{18}			
	Si-O(4)	1.623 (2)Å	1.620 (2)Å
	Si-O(5)	1.628 (3)	1.626 (3)
	Si-O(6)	1.616 (3)	1.620 (2)
	Si-O(7)	1.605 (3)	1.602 (2)
BO_3			
	B-O(2)	1.384 (2)	1.379 (4)
	B-O(8)	1.367 (2)	1.364 (4)
	O(8)-O(2)	2.386 (2)	2.379 (3)
	O(8)-O(8)	2.361 (4)	2.356 (3)
FeO_6			
	Fe-O(1)	2.100 (3)	2.111 (4)
	Fe-O(2)	2.003 (2)	2.003 (2)
	Fe-O(3)	1.954 (2)	1.942 (3)
	Fe-O(6)	1.994 (2)	1.989 (2)

β_{11}(F), $P_n - P_x = 0.19(3)$. The value of $|P_x - P_n|/\sigma$ exceeded 2σ for 4 of the 28 position parameters and for 10 of the 59 thermal parameters. The values of $\Sigma(\Delta/\sigma)^2$ were 81.88 and 145.95 which may be tested as χ^2 with 28 and 59 degrees of freedom. Both values are significant—even if the large contributions of the two parameters cited above are omitted. Thus, there are small systematic differences between the two determinations; these are not however *chemically* significant.

Comparison of some bond lengths, as further examples of the good agreement between the two studies, are presented in Table 5a. We conclude that there are no essential differences in geometry between the two studies.

THE M-AL DISTRIBUTION

The values of the scattering lengths refined for the 18*c* Al and the 9*b* Fe point positions provide values for the occupancy factors of the ions in these sites. Some uncertainty in the chemical analysis reported by Barton (possibly due to occluded SiO_2) should not affect the Fe/Al ratio, although it does affect the total amount of either. We therefore adopt as parameters to be determined: (Al), the total number of atoms of Al in the unit cell; (M), the total number of *M* atoms in the unit cell; *x*, the number of Al atoms in 18*c*; and *y*, the number of *M* atoms in 18*c*. We may write the following equations:

TABLE 6. DISTRIBUTION OF M AND AL BETWEEN THE 9b AND 18c POINT POSITIONS

	Neutrons	X-rays
Al 18c	.936 (13)	.9125 (23)
M 18c	.064 (13)	.0875 (23)
Al 9b	.251 (26)	.2961 (23)
M 9b	.749 (26)	.251 (26)

$$0.35x + 0.898y = 18 \cdot 0.835 = 6.930 \pm 0.13$$

$$0.35[(\mathrm{Al}) - x] + 0.898(0.414(\mathrm{Al}) - y) = 9 \cdot 0.763 = 6.867 \pm 0.10.$$

(The M/Al ratio from the chemical analysis is 0.414.) Solution of these equations gives the following results:

$$(\mathrm{Al}) = 19.11(22)$$

$$(M) \equiv 0.414(\mathrm{Al}) = 7.91(8)$$

for a total of 27.0 atoms and no vacancies in either point position.

$$x = 16.85(23)$$

$$y = 1.15(24)$$

The population in 9b is accordingly

$$\mathrm{Al}_{2.26}M_{6.74}.$$

These values agree, within two standard deviations, with the values determined by Barton. The percentage occupancies are given in Table 6. The agreement is again reasonable. It should be noted that Barton's quoted standard deviations do not take into account the considerable uncertainties in these values due to the uncertainties of the chemical analysis; his 9b M occupancy changed from 0.78 to 0.70 on revision of the chemical analysis.

MAGNETIC STRUCTURE

Magnetic susceptibility measurements (Tsang, Thorpe, Senftle, and Donnay, 1970) indicate that buergerite has an exchange constant $J/k = 7.5°\mathrm{K}$. Donnay *et al.* (1967) have suggested that antiferromagnetic ordering in tourmalines could consist of a trigonal arrangement of spins on iron atoms lying in the mirror plane. X-ray data indicate no structural transition down to 8° K.

We have measured neutron-diffraction powder pattens of buergerite at 295°K and 4.2°K. The patterns are essentially identical (Figure 3). No

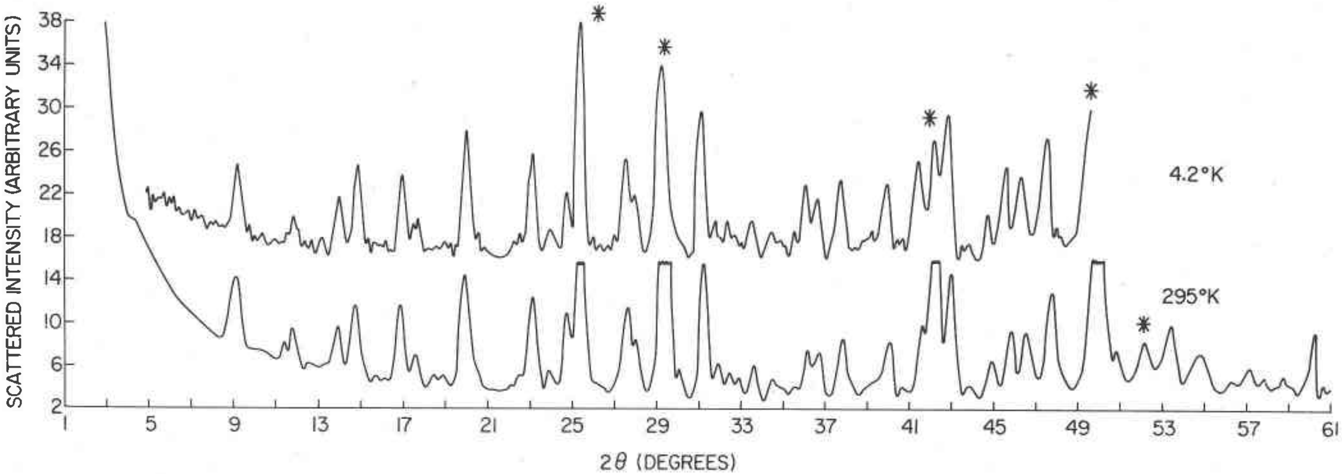

FIG. 3. Neutron powder patterns of buergerite at 4.2°K and 295°K. The low temperature pattern has been given an arbitrary vertical displacement; this pattern was run more quickly and hence has a greater noise level in the background. The peaks marked with asterisks are Al powder lines from the sample holder and cryostat. The neutron wavelength was 1.026 A.

new peaks appear, and there are no significant changes in the intensity of any peaks. We conclude that there is no significant long range magnetic order in buergerite down to 4.2°K. Such order should give rise to appreciable changes in scattered neutron intensity in the Bragg peaks. The observation that there is no change in this intensity does not preclude *local* spin ordering of the type proposed by Donnay *et al.*

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