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The Crystal Structure of Danburite: A Comparison with Anorthite, Albite, and Reedmergnerite

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Abstract

The crystal structure of danburite ($CaB_2Si_2O_8$; a = 8.038 Å; b = 8.752 Å; c = 7.730 Å; space group *Pnam*) has been refined to an unweighted residual of R = 0.021 using 1076 nonzero structure amplitudes. It consists of a tetrahedral framework of ordered B_2O_7 and Si_2O_7 groups which accommodates Ca in irregular coordination ($\langle Ca^{IX}–O \rangle$ = 2.585 Å; $\langle Ca^{VII}–O \rangle$ = 2.461 Å). A 7-fold coordination model appears to be more consistent with structurally similar anorthite, reedmergnerite, and albite as evinced by the linear relationship between the mean Na/Ca–O bond lengths and the mean isotropic temperature factors of Na and Ca in these structures. The mean T–O bond length is 1.474 Å for the B-containing tetrahedron and 1.617 Å for the Si-containing tetrahedron, both of which are somewhat longer than those in reedmergnerite ($NaBSi_3O_8$).

The trends observed between tetrahedral bond lengths, coordination number and Mulliken bond overlap populations for Si–O→Al and Al–O→Si bonds in anorthite are similar to those observed for Si–O→B and B–O→Si bonds in danburite; shorter bonds with larger overlap populations and smaller coordination numbers are involved in wider tetrahedral angles.

Introduction

The crystal structure of danburite, $CaB_2Si_2O_8$, was determined by Dunbar and Machatschki (1931) who described it as a framework of corner-sharing Si_2O_7 and B_2O_7 groups with the Ca atoms coordinated by eight oxygens. Because they had been unable to determine the positions of the boron atoms precisely, Johansson (1959) refined the structure using 538 intensities measured by film methods in a partial three-dimensional least-squares synthesis. His refinement confirmed the structure and yielded bond lengths with e.s.d.'s < 0.02Å. Concurrently Bakakin, Kravchenko, and Belov (1959) completed a similar analysis with poorer results. A study of the nuclear magnetic resonance spectrum of ^{11}B established that B–Si order persists in danburite up to its decomposition temperature (Brun and Ghose, 1964).

This study was undertaken to determine more precisely the bond lengths and angles of danburite (Phillips, Ribbe, and Gibbs, 1971) for comparison with topologically similar paracelsian ($BaAl_2Si_2O_8$) and hurlbutite ($CaBe_2P_2O_8$) and with structurally similar feldspars: anorthite ($CaAl_2Si_2O_8$) and its hexagonal polymorph; celsian ($BaAl_2Si_2O_8$); synthetic $SrAl_2Si_2O_8$; albite ($NaAlSi_3O_8$); and reedmergnerite ($NaBSi_3O_8$). This is part of an extensive investigation of bonding in these structures directed toward a rationalization of their topologies and the steric details and distribution of the tetrahedral atoms (*cf* Ribbe, Phillips, and Gibbs, 1973; Gibbs, Louisnathan, Ribbe, and Phillips, 1973).

Experimental Procedure

A small cleavage fragment (0.10 × 0.17 × 0.23 mm) was taken from a large danburite crystal from San Luis Potosi, Mexico. The specimen is part of the C. A. Michael Collection of Gems and Minerals at V.P.I.S.U. Single crystal photographs were consistent with Bakakin, Kravchenko and Belov's (1959) choice of space group *Pnam*. They state that a statistical test of intensities indicated that danburite is centrosymmetric. Counter diffractometer measurements of 4θ along the axial zones were used to determine the unit cell dimensions: a = 8.038(3); b = 8.752(5); c = 7.730(3)Å.

Intensity data were collected on a Picker automated four-circle diffractometer, using Nb-filtered Mo radiation and a scintillation counter. A computer program written by C. T. Prewitt was used to correct the intensity data for background and Lorentz-polarization effects and to convert to $|F_{obs}|$. Absorption and extinction corrections were consid-

Table 1. Observed and Calculated Structure Factors for Danburite*

h	l	k	F(obs)	F(calc)
3	1	2	11.59	8.54
1	1	7	11.93	11.21
8	0	5	13.52	8.87
7	0	8	13.75	11.44
1	1	12	14.83	15.51
3	1	6	14.85	14.45
3	3	7	15.20	10.90
3	3	8	15.39	10.04
9	1	9	15.44	12.90
3	1	9	15.45	14.96
3	1	5	15.57	14.10
3	0	7	15.63	6.70
1	3	1	15.98	20.47
3	3	9	16.21	11.93
1	7	5	16.23	15.66
4	4	12	16.23	13.60
1	1	9	16.42	17.47
2	4	12	16.59	13.93
6	1	11	16.63	12.54
2	1	8	16.68	12.41
10	2	4	16.83	19.92
0	3	11	16.84	12.93
7	2	4	17.03	20.67
11	4	5	17.12	18.60
9	3	5	17.17	21.82
1	1	6	17.24	15.00
8	3	3	17.54	16.04
1	4	14	17.55	15.90
3	8	9	17.61	21.95
8	4	12	17.61	18.52
12	4	3	17.71	10.97
10	1	3	17.76	21.16
3	2	6	17.78	15.59
7	5	5	17.94	16.51
5	5	12	17.97	14.74
5	7	10	17.99	18.15
7	1	3	18.06	20.43
1	1	11	18.09	18.60
4	4	4	18.23	17.12
1	6	6	18.38	21.50
1	1	6	18.51	17.58
2	2	10	18.55	15.54
3	3	12	18.55	18.27
1	4	5	18.55	15.19
3	3	4	18.58	21.42
3	3	4	18.61	17.77
8	7	2	18.81	15.65
2	11	6	19.07	21.41
8	1	8	19.09	21.89
9	0	8	19.26	12.84
1	1	9	19.47	20.61
4	10	5	19.47	20.66
4	3	9	19.52	18.83
1	1	13	19.62	20.41
11	8	2	19.66	17.84
6	7	9	19.66	13.85
13	0	3	19.87	20.64
5	9	7	19.87	15.74
7	2	7	19.91	17.86
8	4	10	19.98	15.21
11	1	3	19.99	19.13
6	6	4	20.04	21.11
5	10	7	20.11	17.32
3	8	11	20.16	19.85
1	7	10	20.24	18.93
1	1	13	20.32	20.24
7	5	9	20.34	21.58
11	4	1	20.35	21.84
1	6	12	20.47	19.48
1	3	9	20.62	22.22
12	4	1	20.65	19.75
11	9	7	20.71	21.11
4	5	12	20.79	20.29
4	1	2	20.82	16.74
2	1	1	20.82	16.63
10	2	4	20.89	15.50
10	6	4	20.91	14.08
8	2	9	21.06	14.36
7	11	2	21.37	19.51
4	7	4	21.42	20.02
8	3	8	21.46	18.95
1	1	8	21.54	18.62
8	1	4	21.59	22.98
6	0	11	21.74	18.01
8	5	10	21.80	22.39
11	1	3	21.89	21.68
4	7	2	22.25	20.39
1	8	8	22.29	21.47
7	1	6	22.51	25.48
4	4	13	22.62	21.83
9	3	2	22.81	19.63
4	0	11	22.83	21.05
2	6	10	22.84	19.68
7	7	9	22.87	20.59
1	3	8	23.16	22.80
2	11	2	23.22	19.95
4	4	12	23.26	21.28
4	1	13	23.27	23.26
7	6	6	23.28	23.95
2	2	11	23.58	21.54
8	4	7	23.81	21.14
4	2	12	23.85	21.36
2	4	4	23.90	22.73
6	7	4	23.96	22.35
4	4	9	24.00	24.98
1	3	12	24.16	20.56
11	2	1	24.18	22.82
8	5	8	24.56	24.07
7	6	8	24.67	23.39
6	10	6	24.72	21.27
5	11	5	24.83	25.51
1	1	14	24.84	21.45
8	7	4	24.89	23.43
7	8	8	25.11	23.85
4	0	8	25.17	23.11
4	10	5	25.23	23.44
5	3	6	25.63	21.15
4	4	8	25.94	26.72
4	11	1	26.02	25.76
10	5	3	26.14	25.16
10	3	4	26.47	20.31
1	8	9	26.51	28.18
1	1	12	26.52	25.08
8	4	6	26.66	22.49
4	2	2	26.93	22.71
3	6	8	26.96	24.57
9	1	6	26.97	29.94
3	11	6	26.97	23.13
9	3	6	26.98	24.39
7	1	9	27.09	24.56
11	0	3	27.22	28.15
7	1	11	27.40	28.33
4	12	0	27.55	28.37
5	9	2	27.58	27.16
3	6	3	27.61	30.03

h	l	k	F(obs)	F(calc)
0	7	11	27.62	26.52
11	7	2	27.72	26.28
3	7	6	27.73	28.72
9	1	3	27.84	28.62
6	1	5	27.99	25.21
3	7	7	28.12	25.72
5	11	2	28.12	28.88
6	8	1	28.21	27.82
8	10	3	28.25	28.67
3	10	5	28.38	28.75
8	2	4	28.63	26.84
8	3	5	28.96	29.79
7	1	14	29.10	28.77
7	4	6	29.13	27.04
6	5	7	29.15	27.42
6	3	1	29.33	23.67
7	10	1	29.38	29.79
9	6	4	29.40	25.33
4	7	4	29.47	26.23
2	5	11	29.48	32.08
9	12	4	29.56	29.79
10	0	7	29.78	28.34
8	9	10	29.85	27.96
3	4	13	30.13	33.29
7	7	3	30.40	27.41
6	2	13	30.42	27.40
8	4	13	30.43	31.24
1	12	1	30.47	26.03
7	1	9	30.51	28.85
8	7	5	30.56	29.16
3	1	9	30.81	31.59
3	11	4	30.84	29.14
11	2	6	30.85	30.27
7	5	10	31.00	28.63
8	2	6	31.05	27.35
3	3	4	31.10	29.72
4	6	11	31.29	28.52
9	3	3	31.35	28.97
5	0	8	31.50	28.30
8	6	7	31.52	32.32
7	3	10	31.72	28.70
5	7	1	31.74	31.17
1	6	6	31.88	28.44
4	4	7	31.92	27.53
1	9	4	31.92	30.77
5	3	4	32.01	29.25
10	6	5	32.05	35.83
0	10	6	32.16	31.01
9	2	10	32.21	32.57
9	4	3	32.22	31.30
3	7	6	32.29	32.53
12	0	4	32.34	30.56
8	9	1	32.41	32.60
12	4	2	32.49	30.48
2	1	5	32.52	30.75
7	7	1	32.61	32.75
6	1	9	32.68	27.28
6	3	7	33.15	32.97
9	9	4	33.28	34.85
10	1	5	33.47	28.73
5	0	11	33.52	31.01
5	1	12	33.53	31.97
11	5	5	33.79	30.88
11	3	3	34.15	33.11
12	1	2	34.19	32.74
8	3	8	34.35	35.98
2	8	3	34.46	33.68
3	7	10	34.64	36.25
2	12	5	34.85	31.46
11	1	1	34.92	35.95
4	7	8	34.92	34.46
6	4	3	35.01	36.12
4	12	3	35.01	31.44
1	10	4	35.07	32.09
12	2	1	35.09	35.49
2	8	6	35.14	36.78
4	9	7	35.55	36.44
5	4	10	35.63	32.97
8	4	1	35.67	36.82
3	2	11	35.67	36.40
0	8	0	35.83	36.85
8	5	4	36.07	36.19
7	5	11	36.17	34.76
7	5	6	36.54	38.52
8	1	2	36.59	33.75
9	4	8	36.59	35.21
10	1	7	36.91	37.60
2	4	6	37.16	34.47
2	12	9	37.17	38.09
3	7	4	37.23	39.28
12	1	3	37.24	33.27
12	4	3	37.37	33.89
9	2	8	37.38	37.76
2	3	7	37.43	36.18
6	8	6	37.75	38.94
10	3	9	37.82	36.19
5	2	10	37.89	36.61
10	0	4	37.99	36.78
7	2	9	38.09	36.65
8	11	3	38.25	37.77
11	4	5	38.30	38.54
3	4	11	38.41	37.39
1	3	12	38.44	36.32
1	12	3	38.45	36.12
8	3	8	38.47	38.22
7	3	5	38.54	37.78
3	2	14	38.58	41.16
7	10	5	38.75	40.80
6	1	10	38.81	38.57
2	12	3	38.84	37.30
1	1	3	38.90	37.30
2	0	6	38.97	36.64
3	4	11	39.00	38.77
10	1	3	39.09	38.09
10	3	2	39.21	37.34
2	8	3	39.38	40.93
8	0	9	39.63	38.06
3	8	11	39.80	39.70
11	2	2	40.02	39.15
4	4	5	40.08	41.74
11	2	8	40.18	39.59
1	4	8	40.18	39.31
11	1	6	40.29	38.81
6	6	7	40.34	37.67
4	9	5	40.35	39.80
7	1	10	40.39	38.38
8	8	2	40.41	38.66
4	8	10	40.58	42.31
10	8	1	40.82	39.71
7	4	5	40.89	39.39
8	4	5	40.90	40.59
9	3	5	41.27	41.77
3	8	4	41.28	39.42
2	0	7	41.39	38.29

h	l	k	F(obs)	F(calc)
12	1	6	41.47	42.72
6	3	3	41.55	39.75
1	5	3	41.64	39.17
6	1	8	41.66	41.86
2	9	3	41.76	41.69
5	10	1	41.86	39.63
10	2	4	41.91	40.47
2	5	7	42.00	40.26
1	1	3	42.11	41.43
3	9	2	42.20	41.04
7	6	2	42.27	42.64
9	8	6	42.39	39.18
4	0	2	42.44	42.38
3	3	10	42.47	42.59
9	7	7	42.48	39.76
3	2	10	42.64	38.23
7	6	2	42.74	40.12
2	7	0	42.88	41.98
7	5	6	43.04	42.96
3	5	6	43.19	40.83
1	6	10	43.31	38.93
10	4	3	43.52	44.17
3	9	7	43.55	43.73
4	6	1	43.57	43.28
1	8	8	43.60	41.81
3	2	5	43.65	44.62
7	8	6	43.66	42.50
3	5	9	43.69	41.73
4	7	8	43.72	41.73
4	4	1	43.87	47.42
8	10	3	43.89	45.83
3	11	7	43.95	41.61
3	0	11	44.03	44.21
2	11	7	44.04	41.82
6	8	3	44.09	46.00
12	3	0	44.10	42.92
4	11	3	44.25	41.82
12	1	4	44.35	45.47
7	3	6	44.48	43.88
3	2	6	44.52	42.86
1	2	14	44.54	44.80
8	1	10	44.71	45.14
3	8	2	45.13	46.53
8	7	7	45.17	42.38
10	2	2	45.52	46.30
9	8	2	45.53	43.34
5	11	3	45.74	45.40
2	10	8	45.80	43.12
9	10	4	45.86	45.44
1	11	4	45.88	46.73
9	5	8	45.99	44.89
0	8	4	46.02	45.66
11	3	5	46.03	46.72
12	5	0	46.07	47.32
3	9	9	46.10	41.49
4	6	1	46.16	42.39
5	9	0	46.27	46.32
6	7	6	46.61	48.50
8	4	8	46.72	43.71
7	3	9	46.73	46.19
8	1	3	46.83	46.12
11	3	5	47.01	49.67
0	6	8	47.19	46.93
1	12	1	47.31	47.13
6	11	4	47.56	45.60
11	7	3	47.56	47.56
12	6	8	47.68	48.37
1	6	5	47.71	49.66
11	6	1	47.73	48.57
10	3	3	47.93	49.08
4	10	4	47.95	44.21
1	7	8	48.17	50.77
6	8	6	48.29	48.59
7	3	7	48.41	45.65
3	1	14	48.42	49.07
6	11	11	48.51	46.96
10	4	8	48.59	47.75
4	4	12	48.68	48.33
5	9	8	48.78	49.36
1	11	6	48.95	48.16
6	7	6	48.98	51.02
4	6	3	49.20	48.54
1	4	9	49.33	48.77
1	8	7	49.58	47.98
1	9	3	49.79	48.37
10	2	7	49.84	49.06
4	3	5	49.85	50.62
3	7	7	49.88	50.31
3	4	6	50.00	50.75
7	3	9	50.02	51.05
1	6	13	50.05	49.55
2	8	11	50.32	51.21
1	1	11	50.38	50.62
3	0	9	50.42	51.39
3	3	5	50.42	47.49
2	4	5	50.44	46.65
4	1	1	50.46	48.35
3	4	1	50.60	48.87
6	0	3	50.63	47.87
1	11	5	50.74	50.95
8	8	6	50.74	49.15
3	8	10	50.84	49.36
6	1	5	50.96	51.25
9	0	6	50.99	51.44
4	2	4	51.00	50.80
3	1	10	51.06	49.20
1	10	1	51.23	51.62
1	8	4	51.29	50.05
7	1	4	51.38	51.66
4	4	4	51.39	50.43
11	7	1	51.61	50.82
4	5	5	51.66	50.41
5	1	7	51.75	51.63
7	8	8	51.94	51.31
7	6	3	51.95	49.39
5	1	11	52.26	51.79
3	3	14	52.54	54.78
4	8	10	52.66	51.84
10	2	4	52.68	54.19
7	0	3	52.71	50.89
7	5	8	52.71	51.91
3	4	7	52.73	51.11
4	5	8	52.88	52.62
7	11	1	52.99	52.42
1	0	12	53.09	52.65
4	3	5	53.17	55.06
0	8	7	53.21	52.27
1	4	6	53.24	53.51
1	2	8	53.27	53.31
3	5	4	53.30	54.94
4	3	9	53.43	49.46
4	3	5	53.43	51.84
3	3	1	53.47	53.35
6	10	3	53.90	52.39
1	8	6	53.92	51.09

h	l	k	F(obs)	F(calc)
1	8	13	54.08	52.84
8	6	6	54.11	52.93
10	4	8	54.17	51.55
8	6	8	54.24	53.67
5	4	3	54.40	56.17
4	3	1	54.54	51.28
1	8	3	54.55	52.16
0	5	5	54.59	55.94
3	1	12	54.69	55.37
2	5	4	54.77	57.62
4	4	10	54.84	55.43
1	0	3	54.95	54.30
3	3	10	55.20	54.11
5	3	11	55.45	53.77
2	10	7	55.49	58.69
1	8	9	55.54	56.73
6	5	0	55.57	59.17
4	5	6	55.74	56.43
1	5	6	55.83	55.93
4	4	10	55.98	58.81
1	7	8	55.98	54.81
8	8	3	55.98	56.92
1	5	10	56.03	57.57
11	5	6	56.06	55.61
4	5	6	56.22	57.01
1	2	10	56.52	54.95
8	3	5	56.61	56.58
6	6	4	57.17	60.58
1	1	9	57.47	56.76
8	1	11	57.64	59.23
1	4	7	57.73	57.80
7	1	11	57.98	58.02
6	7	9	58.02	60.51
6	4	1	58.09	57.91
6	7	5	58.20	59.83
5	11	1	58.28	58.17
1	5	12	58.32	58.30
2	8	8	58.41	53.55
5	3	10	58.72	57.86
1	5	4	58.72	57.40
1	7	1	58.95	60.52
2	1	8	59.10	59.18
6	6	10	59.30	56.82
3	7	2	59.66	58.61
3	10	6	59.82	59.76
11	5	3	59.92	59.09
4	0	14	59.94	60.14
4	10	4	60.36	59.93
2	1	6	60.52	58.36
1	9	3	60.65	59.26
9	3	8	60.96	62.52
6	0	9	61.09	61.89
8	8	11	61.13	63.05
7	7	4	61.18	58.81
1	4	8	61.22	61.49
3	8	10	61.42	62.25
6	8	1	61.44	60.85
6	1	1	61.80	61.98
7	2	7	61.96	61.63
6	1	1	61.98	63.14
5	6	6	62.02	62.39
2	1	11	62.13	62.43
5	5	12	62.40	63.88
6	8	4	62.53	64.44
1	1	8	62.73	60.33
1	1	7	63.14	62.39
8	6	6	63.17	61.28
9	3	2	63.27	63.59
7	8	8	63.27	64.69
6	0	9	63.29	60.57
2	5	12	63.32	63.59
4	6	6	63.56	58.36
8	5	2	63.84	61.29
2	5	0	64.00	64.50
4	3	12	64.51	66.23
2	10	1	64.52	65.96
5	1	3	64.59	62.54
1	6	6	64.67	62.95
2	0	12	64.68	64.43
10	5	4	64.89	64.67
8	6	7	65.05	64.30
11	0	1	65.08	65.40
3	7	2	65.19	62.97
1	8	9	65.34	64.66
7	10	3	65.39	66.47
10	8	1	65.42	64.05
3	1	11	65.48	66.09
6	5	8	65.56	67.58
6	10	4	65.71	63.28
0	5	9	65.74	67.12
1	5	13	65.84	64.75
3	3	11	65.97	63.87
4	5	12	65.98	65.15
5	5	11	66.41	67.23
6	4	1	66.44	64.05
4	10	3	66.69	65.92
9	9	1	66.70	63.26
7	3	3	67.19	66.15
11	3	2	67.56	66.82
4	6	6	67.63	65.63
12	0	5	67.71	66.03
7	7	11	67.92	67.52
2	8	9	68.34	70.19
3	10	2	68.70	68.81
1	12	4	68.75	65.60
1	1	5	68.86	69.64
1	5	8	68.91	71.00
3	8	11	69.03	70.23
0	8	4	69.38	68.27
2	8	10	69.54	68.48
2	3	2	69.55	70.98
2	5	6	69.56	67.68
12	0	3	69.71	68.49
4	3	5	69.98	67.35
12	5	7	70.01	69.59
8	8	7	70.11	70.28
5	8	10	70.26	70.34
6	0	7	70.29	69.38
10	2	7	70.33	71.81
1	0	8	70.34	70.02
1	4	7	70.44	70.40
13	1	2	70.83	70.78
10	4	5	70.87	72.17
4	5	4	71.01	71.55
4	7	5	71.15	68.05
1	11	7	71.44	70.83
1	4	2	71.46	70.46
1	2	2	71.48	68.69
8	1	1	71.49	71.33
4	8	0	72.20	69.59
7	9	5	72.30	74.87
2	10	10	72.31	71.14
5	9	10	72.38	74.36
4	6	6	72.60	73.62

h	l	k	F(obs)	F(calc)
3	8	6	72.65	70.75
11	1	7	72.70	75.31
10	0	1	72.78	71.23
3	4	5	72.84	71.26
4	3	11	72.90	73.46
3	9	8	72.99	72.58
1	5	12	73.27	74.48
2	0	9	73.44	74.51
10	3	6	73.60	73.27
8	8	0	73.60	72.89
1	4	5	73.65	72.85
8	5	5	73.81	74.36
10	1	2	74.15	75.80
1	8	2	74.35	78.11
10	6	3	74.45	76.11
6	5	3	74.50	72.53
1	2	2	74.52	79.27
8	7	8	74.71	73.36
4	3	5	74.78	73.91
1	8	2	74.88	73.01
3	10	8	74.90	74.36
2	3	14	75.01	77.63
0	10	2	75.01	73.46
4	7	11	75.12	75.22
6	7	10	75.32	73.43
0	9	3	75.50	76.52
9	6	7	75.51	76.91
8	1	12	75.52	78.20
5	8	9	76.16	74.46
6	11	2	76.29	77.07
3	8	6	76.32	78.03
8	2	1	76.64	77.75
8	0	10	76.66	78.19
8	3	12	77.15	76.44
2	9	2	77.30	78.77
9	3	6	77.34	75.02
10	7	1	77.55	78.26
10	5	2	77.60	76.78
3	1	7	77.79	78.11
9	9	2	78.03	78.62
3	4	6	78.41	78.97
2	7	3	78.41	77.86
5	3	11	78.60	81.00
8	5	7	78.60	77.72
12	3	0	79.23	80.12
8	8	0	79.33	82.18
5	1	13	79.47	81.11
8	8	1	79.76	77.81
6	8	2	79.79	81.49
3	4	5	79.81	79.52
4	2	3	79.83	75.67
7	1	5	80.64	81.46
2	5	10	81.51	82.18
3	6	9	81.51	80.98
3	3	10	81.55	84.03
11	0	8	81.66	82.44
10	4	3	81.70	82.81
3	3	9	81.74	83.13
6	9	6	82.10	82.04
10	1	1	82.63	82.40
2	2	12	82.97	80.92
7	8	6	83.15	84.00
11	0	7	83.20	81.28
3	4	10	83.25	83.79
1	4	8	83.29	82.28
3	1	8	83.34	83.64
8	1	4	83.35	83.33
6	3	6	83.44	85.13
5	2	3	83.54	83.91
2	2	1	83.61	85.19
6	10	1	83.64	83.23
4	8	2	83.70	82.00
4	3	7	83.76	85.63
1	7	7	83.87	80.64
6	4	0	84.06	84.45
4	10	0	84.13	84.04
2	11	1	84.35	84.80
1	8	8	84.36	86.20
11	2	5	84.43	85.67
10	3	8	84.65	85.28
3	8	3	85.07	81.94
2	1	4	85.31	81.93
8	8	6	85.39	84.46
13	1	4	85.41	86.90
2	6	1	85.53	81.69
2	6	5	85.70	85.15
8	2	2	85.78	88.31
4	8	2	85.97	86.87
3	10	4	86.17	84.71
0	3	11	86.18	82.29
6	2	1	86.33	84.97
1	3	14	86.49	88.62
11	2	2	86.72	86.75
8	2	5	86.73	87.06
1	7	7	86.74	86.24
4	3	1	86.77	83.73
1	0	7	86.83	89.59
4	10	2	86.99	87.60
1	3	3	87.21	85.97
5	1	7	87.29	85.16
2	6	6	87.46	84.28
8	7	1	87.62	85.98
4	10	7	87.67	88.87
2	6	4	87.85	82.96
10	1	9	88.11	87.59
5	10	2	88.14	86.73
3	10	7	88.25	88.93
2	2	8	88.28	87.74
4	2	7	88.39	85.71
10	7	6	88.47	90.45
3	3	8	88.82	90.29
2	0	14	88.95	90.84
1	1	4	89.12	86.57
9	6	7	89.19	88.67
8	7	7	89.23	89.96
5	1	8	89.29	89.01
5	3	8	89.42	89.27
7	2	5	89.50	88.47
7	6	2	90.04	87.14
5	6	3	90.15	85.21
0	6	12	90.27	93.14
3	5	2	90.34	89.03
4	11	1	90.89	89.13
2	0	11	91.01	91.12
3	5	2	91.41	95.34
10	0	3	91.93	92.06
10	0	6	91.95	91.15
1	1	6	92.11	89.59
3	4	7	92.49	92.23
8	1	11	93.02	94.40
4	9	9	93.03	92.94
10	4	0	93.07	93.14
3	3	4	93.22	94.21
9	3	4	93.45	95.08
6	3	10	93.50	93.43

h	l	k	F(obs)	F(calc)
1	5	8	93.97	91.52
3	9	1	93.99	93.69
2	6	8	94.05	94.66
10	1	0	94.06	93.58
5	11	4	94.22	93.89
10	5	7	94.25	92.98
5	0	6	94.50	93.62
1	9	1	94.50	93.93
10	4	2	94.61	93.14
5	8	6	94.82	94.55
2	6	9	95.00	94.33
6	8	8	95.01	92.72
10	8	3	95.01	96.35
4	12	1	95.26	94.85
0	3	7	95.30	91.00
1	1	5	95.37	96.66
2	7	12	95.47	93.93
2	6	1	95.50	95.39
5	2	11	95.58	96.70
12	4	8	95.67	96.85
3	11	3	95.74	95.16
6	4	11	95.89	93.60
3	3	5	96.20	94.76
8	1	0	96.38	96.94
2	6	6	96.95	92.77
12	6	1	97.21	97.54
2	9	6	97.34	95.16
10	5	6	97.64	96.47
9	0	3	97.95	98.72
13	0	2	98.06	98.35
9	8	3	98.33	100.36
10	3	3	98.43	97.65
9	4	1	99.19	100.30
10	2	0	99.28	100.39
0	2	10	99.37	98.76
4	6	0	99.72	96.77
13	2	1	99.93	99.53
1	4	6	100.18	101.32
0	5	5	100.30	102.06
3	3	6	100.31	98.24
11	3	8	100.42	98.34
11	1	1	100.62	102.20
7	0	6	101.15	96.83
1	7	11	101.76	102.69
4	9	5	101.78	101.92
7	4	10	101.91	101.57
4	10	1	101.97	102.32
8	0	2	102.12	105.35
0	12	2	102.22	103.15
2	6	11	102.47	102.83
2	0	8	102.54	96.80
13	0	4	102.60	99.73
5	1	1	102.98	99.23
9	0	7	103.01	104.71
11	4	4	103.09	103.54
8	6	1	103.38	102.45
8	2	3	103.43	105.30
2	10	8	103.45	105.03
7	3	4	103.46	103.97
4	0	3	103.67	99.99
6	2	6	103.90	105.86
4	7	6	104.05	105.53
8	3	10	104.71	107.25
8	3	12	105.32	103.39
4	1	3	105.43	107.44
1	9	2	105.53	105.42
5	12	7	105.55	106.47
1	7	6	105.80	106.51
4	4	11	105.85	104.04
8	6	0	105.90	105.93
7	8	3	106.22	106.36
5	8	7	106.41	108.00
3	5	4	106.75	108.18
10	1	6	107.11	106.62
11	3	6	107.71	108.45
0	10	8	107.71	105.77
3	7	2	107.72	106.94
4	7	1	107.82	108.73
10	4	6	107.95	107.94
8	6	2	107.99	109.14
1	8	3	108.11	108.73
1	8	2	108.49	108.82
3	2	9	108.91	110.45
1	4	1	108.99	110.14
0	11	8	109.04	104.88
0	6	10	109.08	111.48
5	5	7	109.13	109.57
4	2	0	109.16	109.71
8	3	0	109.24	110.02
4	5	1	109.92	112.73
7	9	7	109.98	110.71
8	0	2	110.01	106.90
8	6	9	110.42	110.13
7	3	3	110.80	109.10
2	10	3	111.33	113.71
1	8	1	111.33	110.44
7	2	1	111.41	112.78
6	6	8	111.69	110.71
3	7	1	111.91	110.51
10	0	5	112.15	109.82
6	2	2	112.48	109.92
2	0	9	112.55	110.65
7	5	7	113.00	114.93
1	8	3	113.11	112.62
6	0	8	113.13	111.95
2	2	9	113.38	111.27
8	7	3	113.51	114.79
2	2	10	113.57	113.04
5	0	12	113.62	115.43
4	10	6	113.68	111.98
12	2	3	113.73	115.77
5	7	4	113.84	112.65
4	3	3	114.10	115.10
2	8	1	114.96	111.47
1	11	2	114.97	114.59
3	8	1	115.20	117.39
5	10	4	115.32	116.56
6	1	6	115.42	112.06
2	10	5	115.79	117.58
1	9	10	115.82	116.32
2	12	1	115.88	113.99
8	9	0	116.08	117.63
3	4	7	116.26	114.83
2	8	8	116.38	115.83
1	7	12	116.42	117.86
1	5	6	116.66	114.30
5	7	3	116.66	116.20
1	10	3	116.70	116.60
11	5	4	117.10	117.16
2	0	10	117.15	118.01
3	6	10	117.35	118.38
3	10	2	117.51	119.67
6	3	4	117.80	119.40
3	4	1	117.91	116.71

h	l	k	F(obs)	F(calc)
4	1	8	118.65	119.90
4	3	7	118.76	118.01
9	3	6	119.06	118.73
8	7	0	119.37	119.10
7	1	7	119.51	118.63
3	6	8	119.53	117.98
11	6	4	119.96	121.63
4	4	5	120.11	123.85
2	5	7	120.31	120.08
10	0	2	120.42	120.77
7	0	3	120.53	116.29
1	1	12	120.73	121.21
0	13	1	120.91	123.11
6	7	2	120.96	120.95
4	1	9	121.07	120.65
8	6	5	121.15	122.21
5	0	2	121.28	121.84
9	0	1	121.34	120.16
3	5	1	121.34	121.00
6	8	5	121.76	121.07
7	3	4	122.04	121.93
0	4	14	122.15	122.69
6	6	1	122.53	124.44
8	7	1	122.56	123.03
4	1	10	122.73	124.20
6	2	2	122.79	125.66
3	6	7	122.99	125.01
10	3	5	123.16	121.85
7	1	1	123.16	123.69
10	1	1	123.51	124.95
11	3	4	123.53	124.99
3	1	3	123.89	121.53
7	7	3	124.04	123.88
5	3	1	124.15	124.79
8	0	4	124.19	127.00
8	0	8	124.36	121.43
4	5	10	124.45	123.60
8	0	10	124.50	120.42
0	1	11	124.59	123.44
7	8	3	124.68	125.73
6	1	9	124.86	123.56
4	11	0	124.87	128.08
1	7	2	124.91	127.54
1	2	6	125.08	126.69
6	5	6	125.38	124.85
2	5	8	125.76	136.10
3	2	12	126.10	127.00
6	6	9	126.17	125.70
3	7	5	126.38	125.90
8	3	10	127.09	130.89
1	1	10	127.46	127.44
8	5	1	127.60	127.15
1	6	13	127.60	129.13
6	8	7	127.81	128.56
4	9	3	128.41	127.25
8	3	7	128.66	130.83
2	1	6	128.68	123.27
3	10	6	128.68	131.32
8	1	9	128.72	127.93
0	9	5	128.84	129.19
2	3	8	129.03	130.18
12	0	0	129.08	133.57
0	12	0	129.15	128.73
4	7	8	129.20	126.07
12	3	1	129.32	131.00
4	4	1	129.35	134.38
1	8	11	129.47	129.61
7	7	2	130.06	129.18
1	4	10	130.16	128.14
5	5	6	130.44	131.88
7	7	6	131.11	130.05
5	3	2	131.30	133.69
0	8	10	131.35	134.56
7	1	1	131.45	131.60
9	1	4	131.48	130.31
12	0	1	131.54	129.80
2	8	0	131.73	135.40
9	7	2	131.77	134.48
9	2	3	131.87	133.40
1	5	5	132.00	132.89
4	4	0	132.12	127.05
0	0	10	132.18	129.82
4	5	2	132.87	129.17
7	2	6	133.03	130.46
3	8	4	133.27	132.34
4	7	3	133.36	135.95
2	11	0	133.71	135.10
2	0	2	134.19	137.35
5	8	4	134.58	133.65
3	3	13	135.29	137.89
5	7	3	136.56	140.03
3	1	13	136.86	139.27
8	0	3	136.88	139.09
5	6	6	137.10	132.53
6	8	0	137.60	138.20
0	2	11	137.67	137.54
0	1	9	137.72	141.47
4	3	11	137.80	139.35
7	3	2	137.84	138.83
5	8	2	139.36	139.33
9	3	4	139.67	140.63
7	9	1	139.74	141.63
1	8	4	140.05	139.81
7	3	7	140.30	138.92
3	11	3	141.23	144.86
1	1	11	141.58	141.75
3	12	4	141.72	142.25
4	8	6	142.99	140.89
1	0	11	144.24	146.47
9	2	5	144.43	141.73
10	2	0	144.91	145.74
0	2	5	144.98	146.99
2	3	9	145.09	143.13
10	3	7	145.47	145.50
7	0	3	145.98	147.39
6	6	0	146.08	148.27
0	3	9	146.10	146.11
5	0	13	147.22	147.52
1	4	2	147.90	149.27
4	3	8	148.70	149.24
7	5	1	148.96	149.14
10	0	0	149.93	148.59
2	5	8	150.03	150.85
4	0	5	150.39	151.83
1	3	1	150.83	155.16
10	5	1	151.00	151.41
1	4	4	151.58	149.26
4	8	9	152.17	152.44
0	5	7	152.49	150.76
5	2	7	152.51	158.95
1	0	8	152.77	154.40
5	3	5	152.98	150.58
2	4	9	153.18	151.24
0	7	3	153.42	156.25
3	3	11	154.24	154.75

h	l	k	F(obs)	F(calc)
0	4	4	154.52	152.27
5	10	1	154.98	157.53
6	5	2	155.31	156.88
2	10	0	155.93	160.03
2	6	0	156.03	163.36
3	0	10	156.40	155.63
7	2	3	156.49	160.54
5	5	1	156.57	158.78
8	0	1	157.02	157.03
6	0	5	160.25	162.31
4	2	1	160.45	162.21
2	6	3	160.62	160.05
0	4	8	161.34	157.14
0	3	11	161.85	164.24
6	0	7	162.07	163.23
3	6	2	163.09	165.06
6	1	0	163.11	166.88
4	5	9	163.66	163.51
3	1	4	163.97	165.87
3	7	7	164.20	164.35
4	4	6	164.50	164.96
0	4	6	164.66	169.49
1	2	11	165.32	166.06
0	11	3	165.53	166.37
10	3	3	165.83	168.04
1	3	10	166.65	167.25
6	4	5	166.70	171.60
6	4	3	167.18	169.25
3	6	4	167.54	172.48
3	8	8	169.29	170.55
7	0	1	171.25	174.94
4	3	0	171.63	173.77
3	5	3	172.71	172.33
3	0	11	172.81	171.53
8	2	7	172.87	175.47
7	3	5	173.30	171.21
7	10	4	173.45	172.88
0	7	9	176.72	175.88
3	0	6	176.97	179.10
3	2	5	177.17	175.90
7	2	10	178.00	179.73
0	5	1	178.09	178.75
1	8	7	178.11	178.66
6	7	0	178.61	178.43
4	8	1	178.85	176.71
4	2	2	179.00	180.89
4	1	1	179.45	177.55
0	4	2	182.99	189.18
5	7	8	183.00	183.70
1	7	4	183.26	181.33
1	0	13	183.45	189.09
10	8	0	184.30	185.52
3	3	1	184.47	185.79
7	8	2	185.00	187.22
1	3	7	185.67	188.29
3	3	13	185.89	190.10
1	10	5	186.09	186.24
3	5	3	187.16	192.73
3	4	1	188.15	194.65
8	2	9	189.15	189.82
8	2	8	189.85	190.96
3	2	2	192.71	187.69
1	3	4	193.22	193.63
4	5	8	194.31	195.71
4	4	3	195.05	199.72
1	3	6	196.91	200.39
5	3	3	197.48	202.13
3	3	7	200.07	203.40
5	2	4	200.86	202.67
5	4	1	201.17	205.44
1	5	2	201.80	202.71
3	1	1	203.01	197.32
3	0	1	205.14	201.32
2	2	2	205.32	205.48
9	5	4	205.44	208.71
7	6	4	206.45	209.22
0	3	1	207.23	213.13
8	3	9	207.79	211.50
0	2	6	208.75	208.80
3	3	5	209.39	214.47
0	3	5	209.47	206.28
6	2	1	210.12	212.44
2	5	1	212.19	217.53
0	6	8	214.52	214.63
0	1	8	214.65	218.03
4	3	6	215.29	220.20
1	6	3	215.42	221.65
3	3	3	216.74	217.61
6	8	3	218.97	220.92
0	8	4	224.26	226.34
3	3	3	225.51	229.06
6	1	0	225.93	223.98
4	2	6	226.98	235.23
5	0	5	229.41	240.55
11	0	4	232.78	236.69
5	0	1	237.76	240.42
9	3	1	239.49	244.07
1	6	3	243.58	247.91
7	0	4	244.22	246.90
3	3	5	248.40	250.89
1	3	2	248.94	244.02
0	3	1	250.93	253.99
1	2	1	252.22	250.04
0	8	2	252.57	259.14
0	10	0	252.77	262.16
3	3	2	254.20	261.21
2	3	8	255.03	259.96
0	5	3	255.29	254.88
8	3	0	255.55	254.24
8	0	1	257.51	259.29
4	0	0	260.41	253.98
3	0	3	264.00	261.69
3	2	4	264.22	275.09
0	5	5	265.76	276.08
5	1	4	271.56	273.49
0	1	5	272.57	277.28
2	2	3	274.34	280.68
4	3	2	275.86	282.50
3	5	4	276.27	285.96
0	2	2	283.47	282.98
4	3	0	285.77	292.85
2	3	2	290.78	304.07
4	3	2	298.07	309.96
3	0	4	299.19	308.70
2	2	1	299.98	307.97
4	0	3	303.81	308.75
2	3	0	305.28	307.09
1	2	7	315.97	329.22
6	0	8	317.29	322.01
3	5	5	319.97	334.41
0	0	4	324.29	323.48
5	0	4	329.87	334.35
2	2	2	336.22	354.25
0	1	2	352.46	351.98

* The *k* and *l* columns are not in their usual order.

ered unnecessary. An anisotropic least-squares refinement was calculated with 1076 structure amplitudes, ($|F_{obs}| > 4\sigma$), using the program by Busing, Martin, and Levy (1962). The $|F_{obs}|$ were weighted according to the scheme proposed by Hanson (1965) and the variation of $\langle w\Delta F^2\rangle$ over the entire range of $|F_{obs}|$ was minimized as suggested by Cruickshank (1965). The values of $|F_{obs}|$ and F_{calc} are given in Table 1. Atomic scattering factors for neutral atoms were taken from Cromer and Waber (1965). The positional parameters and temperature factors (Table 2), interatomic distances and angles (Table 3), and thermal ellipsoid data (Table 4) were obtained from the final cycle of the anisotropic refinement which yielded an unweighted residual of $R = 0.021$.

Description of the Structure

The asymmetric unit of danburite contains two tetrahedrally coordinated (T) cations (B and Si), one calcium, and five oxygen atoms. Of the latter O(1), O(2), and O(3) are bonded to both Si and B, whereas O(4) and O(5) are the bridging oxygens of the Si_2O_7 and B_2O_7 groups, respectively. The mirror planes normal to c at heights of 0.25 and 0.75 contain the calcium atoms and the bridging oxygens, O(4) and O(5). The structure can be thought of as a continuous framework of alternating B_2O_7 and Si_2O_7 groups with the Ca atoms in either 9-fold coordination ($\langle$Ca–O$\rangle$ = 2.585 Å) or 7-fold coordination ($\langle$Ca–O$\rangle$ = 2.461 Å). The 7-fold coordination model appears to be more consistent with structurally similar anorthite, reedmergnerite, and albite as evinced by the strong correlation between

TABLE 2. Positional Parameters and Temperature Factors for Danburite*

Atom	Positional parameters x	y	z	B(Å^2)
Ca	0.3854(1)	0.0765(1)	1/4	0.42(1)
T1	.2590(1)	.4192(1)	.4201(1)	.31(1)
T2	.0533(1)	.1924(1)	-.0558(1)	.25(1)
O1	.1930(1)	.0680(1)	-.0032(1)	.56(1)
O2	.1263(1)	.3650(1)	-.0433(1)	.49(1)
O3	.3998(1)	.3135(1)	.0781(1)	.47(1)
O4	.5136(1)	.6636(1)	1/4	.60(2)
O5	.1838(1)	.4282(1)	1/4	.54(2)

Atom	Anisotropic temperature factors (× 10^4) β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	18(1)	12(1)	18(1)	-1(1)	0	0
T1	12(1)	9(1)	16(1)	0(1)	0(1)	0(1)
T2	10(1)	7(1)	11(1)	0(1)	0(1)	-1(1)
O1	23(1)	13(1)	29(1)	4(1)	-5(1)	-4(1)
O2	21(1)	12(1)	22(1)	-3(1)	-7(1)	-1(1)
O3	18(1)	16(1)	19(1)	2(1)	3(1)	2(1)
O4	28(1)	23(1)	14(1)	5(1)	0	0
O5	18(1)	26(1)	14(1)	3(1)	0	0

* Estimated standard errors are in parentheses and refer to the last decimal place.

TABLE 3. Interatomic Distances and Angles and Bond Overlap Populations (n) in Danburite*

B-O distances (Å)		n(B-O)	O-O distances (Å)		O-B-O angles (°)
T1-O1	1.479	0.534	O1-O2	2.321	102.5
O2	1.498	0.513	O1-O3	2.419	110.7
O3	1.461	0.545	O2-O3	2.429	110.4
O5	1.456	0.539	O2-O5	2.372	106.9
Mean	1.474		O3-O5	2.406	111.2
Si-O distances (Å)		**n(Si-O)**	**O-O distances (Å)**		**O-Si-O angles (°)**
T2-O1	1.617	0.507	O1-O2	2.672	111.1
O2	1.624	0.549	O1-O3	2.650	110.4
O3	1.611	0.492	O1-O4	2.664	111.1
O4	1.614	0.514	O2-O3	2.574	105.4
Mean	1.617		O2-O4	2.636	109.0
			O3-O4	2.638	109.7

Ca-O distances (Å)		[Mult.]	T-O-T angles (°)	
Ca-O1	2.496	[2]	T1-O1-T2	132.4
O2	2.452	[2]	T1-O2-T2	126.3
O3	2.467	[2]	T1-O3-T2	128.1
O5	2.399	[1]	T2-O4-T2	136.8
O2	3.020	[2]	T1-O5-T1	130.6

* *Estimated standard errors for all distances are 0.001Å and all angles 0.1°.*

TABLE 4. Thermal Ellipsoid Data for Danburite*

Atom	Ellipsoid axis	R.M.S. displacement (Å)	Angles to crystal axes (degrees) X	Y	Z
Ca	1	0.068(1)	82(3)	8(3)	90
	2	.073(1)	90	90	180
	3	.077(1)	8(3)	98(3)	90
T1	1	.060(3)	114(39)	24(39)	91(14)
	2	.063(3)	155(38)	114(39)	81(19)
	3	.069(3)	82(18)	85(14)	9(19)
T2	1	.052(1)	89(6)	19(7)	71(7)
	2	.057(1)	48(23)	76(13)	135(19)
	3	.060(1)	41(21)	103(7)	51(19)
O1	1	.066(2)	112(5)	23(4)	82(4)
	2	.082(2)	137(4)	101(5)	131(4)
	3	.102(2)	125(3)	110(2)	42(3)
O2	1	.062(2)	56(4)	46(7)	63(5)
	2	.075(2)	67(5)	135(7)	54(5)
	3	.094(2)	43(3)	98(3)	132(3)
O3	1	.070(2)	42(11)	101(17)	130(18)
	2	.074(2)	71(17)	138(9)	54(17)
	3	.086(2)	54(5)	50(6)	61(5)
O4	1	.066(3)	90	90	0
	2	.086(2)	46(5)	136(5)	90
	3	.104(2)	44(5)	46(5)	90
O5	1	.066(3)	90	90	0
	2	.076(2)	167(4)	77(4)	90
	3	.102(2)	77(4)	13(4)	90

* Estimated standard errors are in parentheses and refer to the last decimal place.

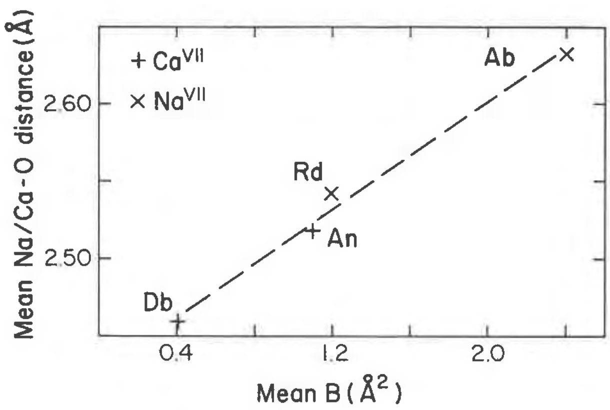

FIG. 1. A plot of mean Ca–O distances for danburite (Db) and anorthite (An), and mean Na–O distances for reedmergnerite (Rd) and albite (Ab) versus the mean isotropic temperature factors for 7-coordinated Ca and Na. Data for Ab and An from Wainwright and Starkey (1968, 1971) and for Rd from Appleman and Clark (1965).

the mean Na/Ca–O bonds lengths and the mean isotropic temperature factors of the Na and Ca atoms (see Fig. 1).

Figure 2 represents a portion of the structure viewed down *c*, showing the 4- and 8-membered rings formed by the alternating B- and Si-containing tetrahedra. Similarities between danburite and feldspar structures were first noted by W. L. Bragg (Taylor, 1933). Both contain double-crankshaft chains (Figure 3A) which consist of 4-membered rings of tetrahedra (Fig. 3B). Within these rings,

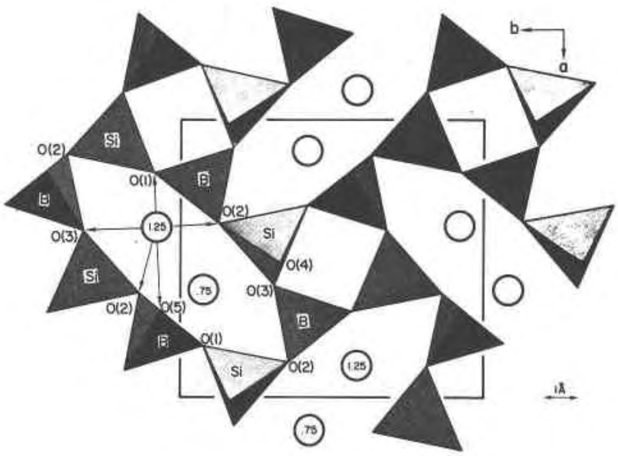

FIG. 2. A portion of the danburite structure viewed down [001] showing the 4- and 8-membered rings formed by the alternating B- and Si-containing tetrahedra. Mirror planes pass through O(4), O(5) and the Ca atoms (open circles) parallel to (001).

two adjacent tetrahedra have apical oxygen atoms that point up (U) and two that point down (D). Figure 3C is a simplified representation of one of these rings in which the oxygen atoms are omitted and the U-D notation of Smith and Rinaldi (1962) is used to describe the orientation of the tetrahedra.

In both feldspar and danburite the 4-membered rings are tilted with respect to the chain axis, which is parallel to *a* in feldspar and *c* in danburite. In the feldspar structure there is also a rotation of successive rings within each chain, although in danburite, which has mirror symmetry perpendicular to the chain axes, no such rotation is possible.

Another point of interest is the cation distribution within a given chain. In danburite, the silicon and boron tetrahedra within a 4-membered ring are always linked to like tetrahedra in mirror-related rings directly above and below in the chain, forming Si–O–Si and B–O–B linkages. Similar linkages are not found in the feldspars, even in anorthite and celsian, which have the same $T^{3+}:T^{4+}$ ratio as danburite. In anorthite, like danburite, there is alternation of T^{3+} and T^{4+} atoms within the layer of 4- and 8-membered rings (Figs. 3D, 3E); however, unlike danburite, there is also a perfect alternation between tetrahedra of subsequent rings within a chain. Thus Al–O–Al and Si–O–Si linkages are not present in anorthite. Anorthite-like alternation of unlike tetrahedral cations is also found in the chains of paracelsian ($BaAl_2Si_2O_8$; Louisnathan, Gibbs, and Craig, in preparation), and hurlbutite ($CaBe_2P_2O_8$; Lindbloom, Gibbs, and Ribbe, in preparation), even though these structures are topologically similar to danburite (Fig. 3E).

Smith and Rinaldi (1962) and Smith (1968) described a number of possible framework structures based on the cross-linking of double-crankshaft chains composed of UUDD 4-membered rings. In the feldspar structure (Fig. 3D) each chain is rotated approximately 180° from the neighboring chains, whereas in danburite (Fig. 3E) successive chains are alternately rotated clockwise and counter-clockwise by approximately 90°. In both anorthite and danburite the 8-membered elliptical rings, which result from cross-linking of the double-crankshaft chains, are characterized by alternation of T^{3+} and T^{4+} tetrahedral cations. In anorthite there are two types of 8-membered rings, UUUUDDDD (elongate parallel to *c**) and UUDUDDUD (elongate parallel to *b**). In danburite only one sequence occurs (UUDUD DUD).

The final structural comparisons concern the stacking of the "layers" shown in Figures 3D and 3E to form the respective feldspar- and danburite-type frameworks. In feldspars the 8-membered rings are underlain by rings of the *different sequence* and *different elongation:* UUUUDDDD rings alternate with UUDUDDUD rings along *a*. In danburite there is only one type of 8-membered ring present; and because there are mirror planes perpendicular to the stacking axis, both sequence and elongation are the same for the rings in successive layers.

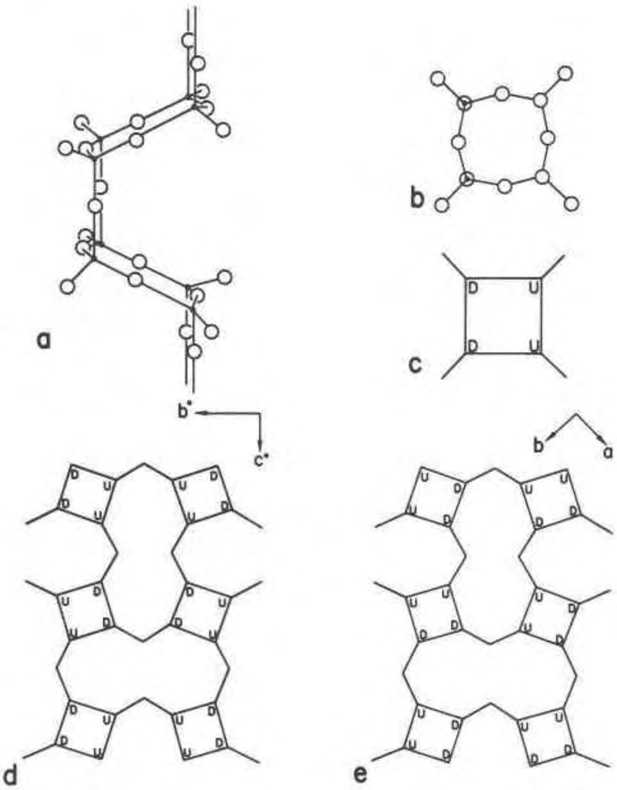

FIG. 3. Schematic representations of portions of the tetrahedral framework: (a) "Jacob's ladder" chain common to danburite and the feldspars (after Taylor, 1933); (b) 4-fold tetrahedral ring, and (c) its symbolic representation (after Smith and Rinaldi, 1962). "U" indicates that the tetrahedron points upward and "D" downward. (d) The arrangement of 4-fold rings of tetrahedra in anorthite resulting in the two types of 8-membered rings (UUUUDDDD elongate parallel to c^* and UUDUDDUD elongate parallel to b^*). (e) Similar arrangement in danburite resulting in only one type of 8-membered ring (UUDUDDUD).

Discussion of Bonding in Danburite and Related Compounds

In a study of anorthite Megaw, Kempster, and Radoslovich (1962) were first to recognize the correlation between the tetrahedral (*T*–O) distances and the coordination number of oxygens involved in the *T*–O bonds. Fleet, Chandrasekhar, and Megaw (1966) found that in bytownite the Na/Ca–O and the *T*–O distances are also inversely correlated. To take into account both the coordination number of oxygen, CN(O), and the distances to the bonded non-tetrahedral cations, Phillips, Ribbe, and Gibbs (1972, 1973) introduced the parameter $\Sigma[1/(\text{Ca–O})^2]$, where Ca–O represents the Ca-oxygen bond length. Since the oxygens in anorthite are bonded to either 0, 1 or 2 calcium atoms, $\Sigma[1/(\text{Ca–O})^2]$ will have the values of zero, $1/(\text{Ca–O})^2$ or $\sum_{2} [1/(\text{Ca}_i\text{–O})^2]$, respectively. As expected, this parameter is strongly correlated with individual tetrahedral bond lengths, giving correlation coefficients of 0.84 for Al–O and 0.90 for Si–O distances. Moreover, when the *T*–O–*T* angles (linearized by the inverse cosine function, $-1/\cos(T\text{–O–}T)$) were included in multiple linear regression analyses, the correlation coefficients increased to 0.89 and 0.94, respectively (Ribbe *et al*, 1973).

The trends observed between bond lengths and coordination number can also be rationalized in terms of overlap integrals, *S*, and Mulliken bond overlap populations, *n*. Interrelationships of bond lengths, coordination number, and overlap integrals for carbon containing compounds have been established by Coulson (1951) and are presented in Figure 4a. The largest overlap integral is calculated for 2-coordinated bonded carbon (sp hybridization) which indicates that bonds involving 2-coordinated atoms should be shorter than those involving 3-coordinated (sp^2 hybridization) or 4-coordinated bonded carbon (sp^3 hybridization). Similar relationships are observed in anorthite, $CaAl_2Si_2O_8$ (Fig. 4b), where shorter Al–O→Si and Si–O→Al bonds have larger Mulliken bond-overlap populations on the average as well as smaller values of CN(O). It is not surprising that in structurally similar danburite, $CaB_2Si_2O_8$, the same trends are found for Si–O→B and B–O→Si linkages (Fig. 4b).

In a study of Mulliken bond-overlap populations in feldspar structures, Gibbs *et al* (1973) found that $n(T\text{–O})$ values calculated assuming constant *T*–O distances correlate with observed *T*–O bond lengths and O–*T*–O and *T*–O–*T* angles for Al- and Si-containing tetrahedra. The shorter *T*–O bonds had larger overlap populations and were involved with wider O–*T*–O and *T*–O–*T* angles. They also calcu-

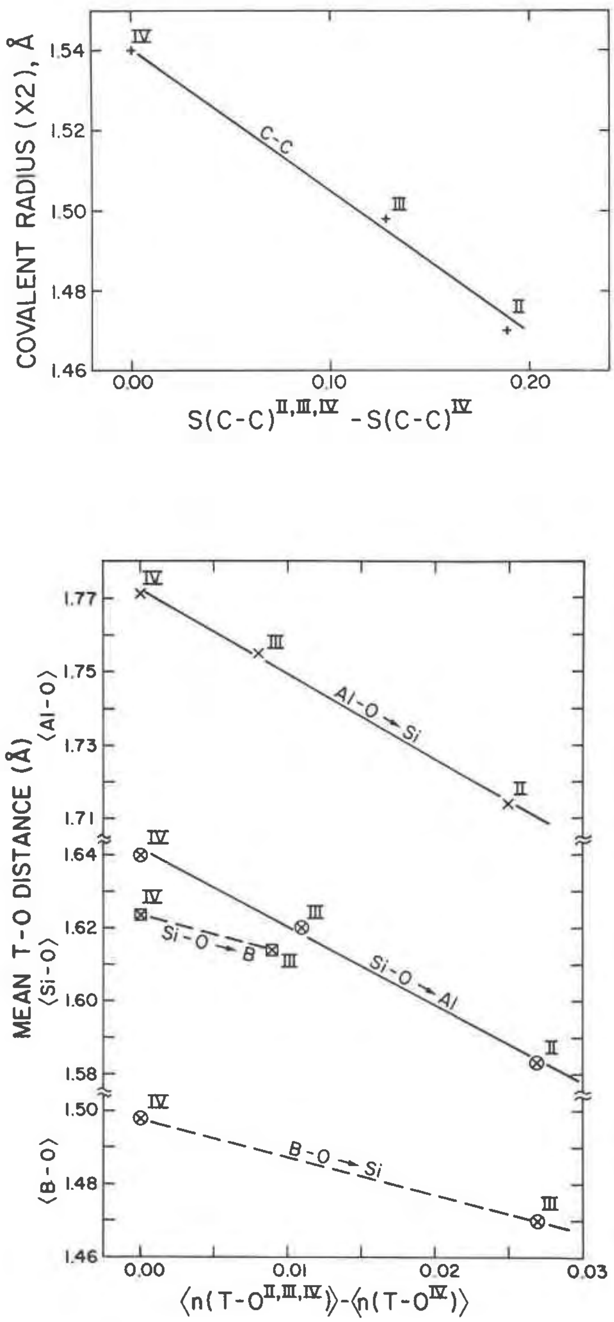

FIG. 4. (a) The differences in the overlap integrals, S, for a C–C bond involving a 4-coordinated carbon atom and those involving 4-, 3- and 2-coordinated carbon atoms versus C–C bond length. (b) The differences in the mean Mulliken bond overlap populations for *T*–O bonds involving a 4-coordinated oxygen atom and those involving 4-, 3-, and 2-coordinated oxygen atoms plotted against mean *T*–O distance in Å. Anorthite data are connected by solid lines, danburite by dashed lines. Roman numerals indicate coordination number.

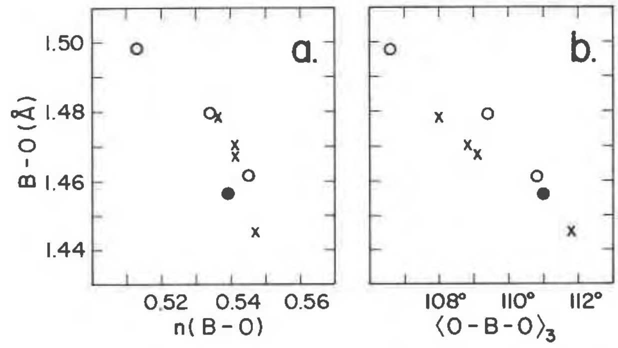

FIG. 5. Individual B–O bond lengths versus n(B–O) and $\langle$O–B–O$\rangle_3$ for danburite (B–O→Si, open circles; B–O→B, filled circles) and for reedmergnerite (B–O→Si, X's).

lated $n(T$–O) for the B-tetrahedron in reedmergnerite, $NaBSi_3O_8$, but correlations with observed bond lengths and angles were not attempted at that time because of the paucity of data. These are plotted here in Figures 5a and 5b with similar data for the B-tetrahedron in danburite. The correlations of observed B–O distances with n(B–O) and the average O–B–O angle involving a common B–O bond, $\langle$O–B–O$\rangle_3$, are well developed in the expected manner with shorter bonds involving larger overlap populations and wider tetrahedral angles.

Ribbe *et al* (1973) have demonstrated the importance of the effect of CN(O) on bond lengths in *T*–O–*T* linkages in the feldspars: *T*–O bonds to oxygens of different coordination numbers should be treated as separate populations. Correlations of B–O with B–O–Si angle for CN(O) = 4, 3, and 2 in danburite and reedmergnerite were found to be indeterminate, because there are only two 4-coordinated, four 3-coordinated, and one 2-coordinated oxygen atoms in these structures.

Inasmuch as danburite will be included as part of an extensive investigation of the crystal chemistry and bonding in $MT_2^{3+}T_2^{4+}O_8$ and $MT_2^{2+}T_2^{5+}O_8$ compounds currently underway in our laboratory and in the Institut für Mineralogie at Westfälische Wilhelms-Universität in Münster, Germany, and the Istituto di Mineralogia e Geochimica at the University in Torino, Italy, further discussion of the structure will be deferred to a future report.

Acknowledgments

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References

APPLEMAN, D. E., AND J. R. CLARK (1965) Crystal structure of reedmergnerite, a boron albite, and its relation to feldspar crystal chemistry. *Am. Mineral.* **50,** 1827–1850.

BAKAKIN, V. V., V. B. KRAVCHENKO, AND N. V. BELOV (1959) The crystalline structure of danburite $CaB_2Si_2O_8$ and hurlbutite $CaBe_2P_2O_8$. *Doklady Akad. Nauk SSSR,* **129,** 1155–1158.

BRUN, E., AND S. GHOSE (1964) Nuclear magnetic resonance spectrum of ^{11}B and B–Si order in danburite, $CaB_2Si_2O_8$. *J. Chem. Phys.* **40,** 3031–3033.

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) A Fortran crystallographic least-squares program. *U.S. Nat. Tech. Inform. Serv.* ORNL-TM-**305.**

COULSON, C. A. (1951) Critical survey of the method ionic-homopolar resonance. *Proc. Royal Soc. (London),* **A207,** 63–73.

CROMER, D. T., AND J. T. WABER (1965) Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18,** 104–109.

CRUICKSHANK, D. W. J. (1965) Errors in least-squares methods. In, J. S. Rollett, Ed., *Computing Methods in Crystallography.* Pergamon Press, New York, pp. 112–116.

DUNBAR, C., AND F. MACHATSCHKI (1931) Structure of danburite, $CaB_2Si_2O_8$. *Z. Kristallogr.* **76,** 133–146.

FLEET, S. G., S. CHANDRASEKHAR, AND H. D. MEGAW (1966) The structure of bytownite ('body-centered anorthite'). *Acta Crystallogr.* **21,** 782–801.

GIBBS, G. V., S. J. LOUISNATHAN, P. H. RIBBE, AND M. W. PHILLIPS (1973) Semiempirical molecular orbital calculations for the atoms of the tetrahedral framework in anorthite, low albite, maximum microcline and reedmergnerite. In, W. S. MacKenzie and J. Zussman, Eds., *Proceedings NATO Advanced Study Institute on Feldspars.* Manchester University Press, pp. 49–67.

HANSON, A. W. (1965) The crystal structure of the azulene, S-trinitrobenzene complex. *Acta Crystallogr.* **19,** 19–26.

JOHANSSON, G. (1959) A refinement of the crystal structure of danburite. *Acta Crystallogr.* **12,** 522–525.

MEGAW, H. D., C. J. E. KEMPSTER, AND E. W. RADOSLOVICH (1962) The structure of anorthite, $CaAl_2Si_2O_8$. II. Description and discussion. *Acta Crystallogr.* **15,** 1017–1035.

PHILLIPS, M. W., P. H. RIBBE, AND G. V. GIBBS (1971) Refinement of the crystal structure of danburite [abstr.] *Geol. Soc. Am. Southeastern Sect. 5th Annu. Meet. Blacksburg, Va. May 5–8, 1971, Abstr. Programs,* **3,** 338.

———, ———, AND ——— (1972) Tetrahedral bond length variations in anorthite (rev. abstr.). *Am. Geophys. Union, 53rd Annu. Meet. Washington, D.C. April 17–21, 1972 Program,* p. 48.

———, ———, AND ——— (1973) Tetrahedral bond length variations in anorthite. *Am. Mineral.* **58,** 495–499.

RIBBE, P. H., M. W. PHILLIPS, AND G. V. GIBBS (1973) Tetrahedral bond length variations in feldspars. In, W. S. MacKenzie and J. Zussman, Eds., *Proceedings NATO Advanced Study Institute on Feldspars.* Manchester University Press, pp. 26–48.

SMITH, J. V. (1968) Further discussion of framework structures built from four- and eight-membered rings. *Mineral. Mag.* **36,** 640–642.

———, AND F. RINALDI (1962) Framework structures formed from parallel four- and eight-membered rings. *Mineral. Mag.* **33,** 202–212.

TAYLOR, W. H. (1933) The structure of sanidine and other feldspars. *Z. Kristallogr.* **85,** 425–442.

WAINWRIGHT, J. E., AND J. STARKEY (1968) Crystal structure of a metamorphic low albite (abstr.). *Geol. Soc. Am. Abstr. Programs,* **2,** 310.

———, AND ——— (1971) A refinement of the structure of anorthite. *Z. Kristallogr.* **133,** 75–84.

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