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The Crystal Structure of Ussingite

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Abstract

The crystal structure of ussingite, $Na_2AlSi_3O_8OH$, a = 7.256, b = 7.686, c = 8.683Å, α = 90°45′, β = 99°45′, γ = 122°29′, space group $P\bar{1}$, Z = 2, has been determined through direct methods using 1261 intensities measured with an automatic diffractometer. The least-squares refinement led to a final discrepancy index R = 0.028 for 1101 observed reflections. Ussingite is a unique type of aluminosilicate framework structure in which two of the nine oxygens are hydrogen-bonded and the others are bridging oxygens, linking the tetrahedra into a new type of "interrupted" framework (sharing coefficient c = 1.875) containing 4-, 6-, and 8-fold tetrahedral rings. Aluminum is ordered into one tetrahedral site (mean T(1)-O = 1.734 Å) and silicon into the other three non-equivalent tetrahedra (mean T-O = 1.620 Å). One 5- and one 6-coordinated sodium atom are located in irregular cavities in the framework.

Introduction

Ussingite was found for the first time in a pegmatite at Kangerdl[illegible]rsuk, Greenland, and described by Bøggild (1915) who determined the chemical formula as $Na_2AlSi_3O_8OH$. Owing to the lack of well developed crystals, Bøggild could not determine the axial ratios and angles but only the cleavage angles. The cleavages observed by Bøggild are: $c(100)$, $M(1\bar{1}\bar{1})$ and $m(01\bar{1})$; these indices are consistent with the triclinic reduced cell adopted in this work.

Ilyukhin and Semenov (1959) described ussingite from the Lovozero Alkali Massif, U.S.S.R. They confirmed the chemical formula and determined the cell parameters which are related to those of the reduced cell (see below) through the matrix (0 0 1/ 0 1 0/ 1 1 1).

Experimental

A roughly prismatic crystal fragment of ussingite (0.15 × 0.11 × 0.06 mm) from Lovozero was used for the data collection. The cell dimensions and the intensities were measured with a Syntex $P\bar{1}$ automatic diffractometer using Mo$K\alpha$ radiation monochromatized with a graphite crystal.

The lattice parameters are: a = 7.256, b = 7.686, c = 8.683 Å (each ±0.003 Å), α = 90°45′, β = 99°45′, γ = 122°29′ (each ±2′), V = 399.43 Å^3; space group $P\bar{1}$, Z = 2; observed (Bøggild, 1915) and calculated densities are 2.49 and 2.51 g/cc, respectively.

The intensities of all independent reflections in the range 2.5°–50° 2θ were measured using the $\theta - 2\theta$ scan mode; the scan rate ranged from 1.5° to 24°/min. according to intensity; one standard reflection ($\bar{2}\bar{2}2$) was monitored every 15 reflections and its intensity did not change by more than 4 percent. The intensities were scaled on the basis of a scan rate of 1°/min. and were corrected for Lorentz and polarization factors but not for absorption. Of the 1261 experimentally determined reflections, 160 were considered to be "unobserved" as their intensities did not exceed twice the standard deviation of the counting statistics.

The secondary extinction was negligible, so no extinction factor was taken into account. The atomic scattering factors used for Na, Si, Al, and O are those listed by Hanson *et al* (1964); that of hydrogen is given by Stewart *et al* (1965).

Structure Determination and Refinement

The crystal structure was solved by the application of Sayre's equation using the program written by Long (1965). A least-squares isotropic refinement, carried out on the structure amplitudes with a modified version of the program ORFLS (Busing, Martin, and Levy, 1962), reduced the conventional R index from 0.20 to 0.042. At this stage the hydrogen atom was located along the short hydrogen bond occurring between two oxygen atoms by use of a difference synthesis. Three successive least-squares cycles were performed with anisotropic thermal parameters; the atomic parameters of the hydrogen

TABLE 1. Atomic Coordinates and Equivalent Isotropic Temperature Factors for Ussingite*

Atom	x/a	y/b	z/c	B_H (Å^2)
Na(1)	0.1759(2)	0.3924(2)	0.0555(2)	1.79
Na(2)	0.8214(2)	0.2342(2)	0.4421(2)	1.65
T(1) = Al	0.2422(1)	0.0457(1)	0.8551(1)	0.66
T(2) = Si	0.2463(1)	0.1935(1)	0.3626(1)	0.64
T(3) = Si	0.3203(1)	0.4147(1)	0.6924(1)	0.68
T(4) = Si	0.7014(1)	0.1041(1)	0.8129(1)	0.66
O(1)	0.0021(3)	0.1358(3)	0.2792(3)	1.35
O(2)	0.1419(4)	0.4749(3)	0.6515(3)	1.49
O(3)	0.2767(4)	-0.0021(3)	0.3473(2)	1.09
O(4)	0.3010(3)	0.2970(3)	0.8489(2)	1.06
O(5)	0.4442(4)	0.0224(3)	0.7955(3)	1.38
O(6)	0.4231(3)	0.3818(3)	0.2768(3)	1.28
O(7)	0.7980(4)	0.0344(4)	0.9625(3)	1.56
O(8)	0.8580(4)	0.3557(3)	0.8210(3)	1.59
O(9)	0.2973(4)	0.2604(3)	0.5485(3)	1.55
H	0.979(9)	0.405(8)	0.765(6)	4.72

* *Standard deviations in parentheses; equivalent isotropic temperature factors after Hamilton (1959).*

atom were introduced in the structure factor calculations, but were not allowed to vary. The *R* index dropped to 0.030. Two more cycles, carried out by varying the coordinates and the isotropic temperature factor of hydrogen, led to a final discrepancy index $R = 0.028$ for the 1101 observed reflections (0.035 for all reflections).

The final atomic parameters are given in Tables 1 and 2; bond distances and angles are listed in Table 3; the observed and calculated structure factors are compared in Table 4.

Description and Discussion of the Structure

Ussingite is a unique framework alumino-silicate in which two of the nine oxygen atoms are hydrogen bonded and the others are bridging oxygens, linking the tetrahedra into a new type of "interrupted" framework (sharing coefficient $c = 1.875$) containing 4-, 6-, and 8-fold tetrahedral rings (Fig. 1). The basic structural feature of ussingite is a zig-zag chain composed of units of four tetrahedra that repeat translationally along *c* (Fig. 2). Oxygens O(3), O(4), O(7) and O(9) are the bridging atoms between tetrahedra within each chain. The chains are repeated by inversion centers. Each chain is linked to three adjacent ones through the oxygen atoms O(1), O(5) and O(6) to form a three-dimensional network which is interrupted by the non-bridging, hydrogen-bonded oxygens, O(2) and O(8).

The two chains related by the symmetry centers at 0, 0, 0 and 0, 0, 1/2 are linked to each other by the oxygen atoms O(1) to form rings of six tetrahedra (Fig. 3), whereas the two chains repeated by the centers at 1/2, 1/2, 0 and 1/2, 1/2, 1/2 are connected by the oxygens O(6) and form rings of four and eight tetrahedra (Fig. 4). The same situation occurs for the chains related by symmetry centers at 1/2, 0, 0 and 1/2, 0, 1/2 and linked through the oxygens O(5). The four adjacent chains

TABLE 2. Anisotropic Thermal Parameters for Ussingite*

Atom	r.m.s.	$U_i a$	$U_i b$	$U_i c$	Atom	r.m.s.	$U_i a$	$U_i b$	$U_i c$
Na(1)	0.133(3)	57	131	138	O(3)	0.105(6)	73	104	166
	0.147(2)	50	129	53		0.109(6)	128	17	104
	0.169(2)	123	114	73		0.136(4)	136	100	87
Na(2)	0.125(3)	100	57	147	O(4)	0.106(6)	81	90	178
	0.137(3)	125	33	57		0.113(5)	92	31	91
	0.167(2)	144	92	89		0.128(4)	171	59	89
T(1)	0.081(3)	156	81	73	O(5)	0.109(5)	169	68	81
	0.091(3)	73	124	35		0.140(4)	100	34	68
	0.102(2)	73	144	120		0.144(4)	92	66	156
T(2)	0.081(3)	146	91	83	O(6)	0.100(5)	57	72	127
	0.093(3)	121	16	106		0.126(5)	66	91	40
	0.096(2)	77	106	163		0.151(4)	43	162	102
T(3)	0.081(3)	68	69	142	O(7)	0.106(5)	106	63	151
	0.093(3)	73	70	52		0.130(4)	19	124	117
	0.102(2)	28	151	94		0.177(4)	100	134	100
T(4)	0.078(3)	150	68	50	O(8)	0.113(5)	120	117	69
	0.092(2)	60	125	43		0.124(5)	128	42	49
	0.103(2)	95	137	104		0.179(4)	123	60	132
O(1)	0.111(5)	152	84	90	O(9)	0.102(6)	88	91	170
	0.123(5)	118	21	70		0.134(5)	112	10	93
	0.154(5)	90	70	160		0.174(4)	156	80	81
O(2)	0.117(4)	158	48	101					
	0.126(4)	111	116	46					
	0.164(4)	82	127	134					

*Root mean square thermal vibrations along the ellipsoid axes (Å) and angles (°) between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoid.

TABLE 3. Interatomic Distances and Tetrahedral Bond Angles in Ussingite*

Atoms	Distance
Na(1)-O(1)	2.741(3) Å
O(4)	2.411(2)
O(6)	2.432(3)
O(7)	2.613(3)
O(8)	2.691(3)
O(8')	2.346(3)
Average	2.539
Na(2)-O(1)	2.440(3)
O(2)	2.449(3)
O(2')	2.283(3)
O(3)	2.489(2)
O(5)	2.515(3)
Average	2.435
T(1)-O(1)	1.746(2)
O(4)	1.744(2)
O(5)	1.728(2)
O(7)	1.721(2)
Average	1.734
T(2)-O(1)	1.604(2)
O(3)	1.640(2)
O(6)	1.629(2)
O(9)	1.605(2)
Average	1.619
T(3)-O(2)	1.584(2)
O(4)	1.626(2)
O(6)	1.636(2)
O(9)	1.635(2)
Average	1.620
T(4)-O(3)	1.660(2)
O(5)	1.594(2)
O(7)	1.606(2)
O(8)	1.626(2)
Average	1.621
O(2)-O(8)	2.507(3)
O(2)-H	1.54(5)
O(8)-H	0.97(5)

Atoms	Angle
O(1)-T(1)-O(4)	111.8(1)°
O(5)	103.3 "
O(7)	106.2 "
O(4)-T(1)-O(5)	111.6 "
O(7)	111.8 "
O(5)-T(1)-O(7)	111.7 "
O(1)-T(2)-O(3)	113.1(1)
O(6)	106.7 "
O(9)	111.2 "
O(3)-T(2)-O(6)	109.3 "
O(9)	105.1 "
O(6)-T(2)-O(9)	111.4 "
O(2)-T(3)-O(4)	113.7(1)
O(6)	112.2 "
O(9)	111.6 "
O(4)-T(3)-O(6)	106.1 "
O(9)	106.6 "
O(6)-T(3)-O(9)	106.1 "
O(3)-T(4)-O(5)	107.0(1)
O(7)	107.5 "
O(8)	107.7 "
O(5)-T(4)-O(7)	113.7 "
O(8)	111.9 "
O(7)-T(4)-O(8)	108.8 "
T(1)-O(1)-T(2)	144.0(1)
T(2)-O(3)-T(4)	127.3 "
T(1)-O(4)-T(3)	125.9 "
T(1)-O(5)-T(4)	149.0 "
T(2)-O(6)-T(3)	142.6 "
T(1)-O(7)-T(4)	143.7 "
T(2)-O(9)-T(3)	148.9 "
O(2)-H-O(8)	171(3)

* Estimated standard deviations are given in parentheses to immediate right of interatomic distances or bond angles.

TABLE 4. Observed and Calculated Structure Factors for Ussingite*

1	0	0*	2.1	1.9
2	0	0	105.4	-106.9
3	0	0*	0.0	-0.2
4	0	0	31.8	31.3
5	0	0	7.0	-7.6
6	0	0	4.2	4.2
7	0	0	22.5	21.5
0	1	0	28.2	28.3
1	1	0	45.4	-45.1
-1	1	0	35.0	34.5
2	1	0	10.1	8.4
-2	1	0	62.0	-61.8
3	1	0	27.2	27.8
-3	1	0	5.7	-6.7
4	1	0	35.7	36.0
-4	1	0	68.0	67.7
5	1	0	12.4	-13.0
-5	1	0	24.6	25.0
6	1	0	20.6	-20.9
-6	1	0	27.6	-28.0
-7	1	0	9.2	-9.4
0	2	0	26.0	24.2
1	2	0	24.8	25.2
-1	2	0	55.1	-55.5
2	2	0	21.9	-27.5
-2	2	0	32.1	31.3
3	2	0*	1.0	0.9
-3	2	0	9.3	-8.2
4	2	0	15.6	15.5
-4	2	0	14.1	-14.3
5	2	0	20.9	-20.5
-5	2	0	22.9	22.9
-6	2	0	11.6	12.5
-7	2	0	29.0	-29.9
0	3	0	26.3	25.0
1	3	0	29.3	-29.2
-1	3	0	11.7	-9.5
2	3	0	15.0	-15.3
-2	3	0*	1.9	2.4
3	3	0	17.1	-18.0
-3	3	0	7.8	6.5
4	3	0	12.3	12.1
-4	3	0	42.4	-42.6
5	3	0	6.5	6.1
-5	3	0	13.8	-13.6
-6	3	0	8.2	8.2
-7	3	0	10.7	10.9
0	4	0*	0.0	-0.9
1	4	0	20.3	19.8
-1	4	0	28.0	-28.3
2	4	0	11.2	-11.1
-2	4	0	28.1	-27.0
3	4	0	19.4	-19.9
-3	4	0	16.6	-15.9
4	4	0	13.6	13.8
-4	4	0	6.6	5.9
-5	4	0	16.6	16.1
-6	4	0	12.2	-12.6
-7	4	0	17.7	-17.7
0	5	0	30.7	30.6
1	5	0	17.5	-18.4
-1	5	0	11.0	11.1
2	5	0	6.9	-6.8
-2	5	0	29.1	-30.1
3	5	0	4.4	-3.8
-3	5	0	31.7	-31.5
-4	5	0	29.5	29.8
-5	5	0	29.3	29.3
-6	5	0	29.1	-30.1
-7	5	0	17.2	-17.6
0	6	0	14.0	-14.0
1	6	0	11.6	-11.4
-1	6	0	26.3	26.6
2	6	0	19.4	19.0
-2	6	0*	2.1	2.7
-3	6	0	31.7	-31.3
-4	6	0	6.2	5.0
-5	6	0	42.0	43.2
-6	6	0	25.2	-25.4
-7	6	0	15.0	-15.6
0	7	0*	0.0	-0.0
1	7	0	20.7	-20.6
-1	7	0	10.2	10.4
-2	7	0	8.6	8.3
-3	7	0	9.1	9.1
-4	7	0	5.9	5.9
-5	7	0	6.0	5.7
-6	7	0	4.5	4.3
-7	7	0	9.4	-9.4
0	0	1	3.4	-4.0
1	0	1*	0.0	-1.1
-1	0	1	6.1	7.1
2	0	1	7.7	-7.6
-2	0	1	8.7	9.1
3	0	1	8.6	-8.2
-3	0	1	20.1	-19.9
4	0	1	3.4	3.5
-4	0	1*	3.1	-4.1
5	0	1	4.5	-4.0
-5	0	1	15.5	14.9
6	0	1*	0.0	2.0
-6	0	1*	1.1	-1.7
-7	0	1	11.7	-11.3
0	1	1	31.9	31.3
0	-1	1	6.1	5.9
1	1	1	39.6	-41.5
-1	1	1	2.6	-2.1
1	-1	1	33.7	-34.0
1	1	-1	37.1	36.6
2	1	1	34.3	-33.3
-2	1	1	26.0	-25.1
2	-1	1	50.4	51.6
2	1	-1	15.3	-17.9
3	1	1	33.7	33.2
-3	1	1*	0.0	2.9
3	-1	1	19.9	19.0
3	1	-1	39.6	-40.2
4	1	1	22.0	-23.6
-4	1	1	16.8	15.9
4	-1	1	47.5	-48.3
4	1	-1	66.0	67.2
5	1	1	5.6	-4.7
-5	1	1	62.8	-64.3
5	-1	1	29.1	29.9
5	1	-1	16.9	16.5
6	1	1	14.5	13.9
-6	1	1*	0.0	2.2
6	-1	1	7.4	7.4
6	1	-1	31.2	-31.5
-7	1	1	25.4	25.8
7	-1	1	11.4	-11.5
0	2	1	28.9	29.7
0	-2	1	56.2	55.5
1	2	1	3.6	4.6
-1	2	1	52.7	-52.6
1	-2	1	33.1	32.2
1	2	-1	33.1	31.9
2	2	1	16.8	-17.7
-2	2	1	50.1	-49.8
2	-2	1	32.1	-32.7
2	2	-1	22.8	-22.4
3	2	1	31.3	-31.9
-3	2	1	29.3	-27.6
3	-2	1	15.1	12.9
3	2	-1	14.7	-15.3
4	2	1	5.9	5.6
-4	2	1	42.8	41.8
4	-2	1	8.5	9.0
4	2	-1	17.4	17.8
5	2	1	21.1	21.2
-5	2	1	7.9	7.8
5	-2	1	24.7	25.3
5	2	-1	4.4	2.5
-6	2	1	26.0	-26.1
6	-2	1	9.2	8.3
6	2	-1*	3.9	3.6
-7	2	1	3.8	3.7
7	-2	1	21.0	-20.8
0	3	1	77.6	78.6
0	-3	1*	1.6	-1.8
1	3	1	16.3	17.2
-1	3	1*	1.8	-2.4
1	-3	1	25.6	26.0
1	3	-1	9.0	8.8
2	3	1	62.7	-64.7
-2	3	1	44.4	-45.0
2	-3	1	6.4	-5.3
2	3	-1	31.3	31.5
3	3	1	14.4	-14.7
-3	3	1	8.9	-6.7
3	-3	1	66.3	-66.8
3	3	-1	4.1	1.5
4	3	1	23.0	23.4
-4	3	1*	1.7	1.3
4	-3	1	6.9	6.1
4	3	-1*	3.6	-3.0
5	3	1*	0.0	-2.7
-5	3	1	18.0	-18.0
5	-3	1	77.9	77.4
5	3	-1	4.2	-4.6
-6	3	1	6.4	5.6
6	-3	1*	0.0	0.1
-7	3	1	8.3	-9.2
7	-3	1	23.4	-23.9
0	4	1	8.3	7.5
0	-4	1	80.4	-81.1
1	4	1	3.7	2.6
-1	4	1	27.5	-27.2
1	-4	1	26.6	26.3
1	4	-1	41.5	-41.6
2	4	1	6.3	5.8
-2	4	1	20.2	-20.3
2	-4	1	43.4	42.8
2	4	-1	36.3	36.7
3	4	1	15.3	14.9
-3	4	1	17.4	-16.6
3	-4	1	23.6	23.1
3	4	-1	18.8	19.0
4	4	1	7.5	8.7
-4	4	1	70.9	71.6
4	-4	1	28.1	-27.8
4	4	-1	11.2	-12.3
-5	4	1	27.7	28.7
5	-4	1	16.2	16.1
-6	4	1	28.3	-28.2
6	-4	1	7.7	-8.7
-7	4	1	26.5	-26.8
7	-4	1	25.9	-25.4
0	5	1	12.3	12.7
0	-5	1	38.5	-38.5
1	5	1*	2.6	-2.9
-1	5	1	12.8	13.0
1	-5	1	17.4	17.4
1	5	-1	5.3	5.7
2	5	1	9.2	-9.0
-2	5	1	33.6	34.1
2	-5	1	11.6	11.5
2	5	-1	26.3	26.4
3	5	1*	0.0	0.9
-3	5	1	18.0	-18.4
3	-5	1	33.1	-33.0
3	5	-1	14.8	-14.4
-4	5	1	26.7	-25.9
4	-5	1	22.8	-24.0
-5	5	1	42.0	41.8
5	-5	1	7.8	8.1
-6	5	1	15.2	14.6
6	-5	1	9.2	9.7
-7	5	1	31.6	-31.2
7	-5	1	7.8	6.9
0	6	1	6.6	-7.9
0	-6	1	8.7	9.4
1	6	1	11.3	-11.5
-1	6	1	25.2	26.1
1	-6	1	14.8	-15.8
1	6	-1*	2.1	-2.0
2	6	1	10.1	9.8
-2	6	1	22.0	22.3
2	-6	1	4.4	-5.0
2	6	-1	10.7	-10.8
-3	6	1	16.1	-16.5
3	-6	1	16.4	17.2
-4	6	1*	1.1	0.1
4	-6	1	27.1	-28.0
-5	6	1	4.4	3.9
5	-6	1	16.8	-17.4
-6	6	1	10.9	10.2
6	-6	1	4.2	4.3
-7	6	1	4.2	-4.8
7	-6	1	13.2	14.3
0	7	1*	2.7	-2.2
0	-7	1*	1.2	0.8
-1	7	1	8.7	-8.4
1	-7	1	6.9	6.4
1	7	-1	11.7	-12.1
-2	7	1*	3.1	2.9
2	-7	1	41.9	-42.7
-3	7	1	32.3	-33.3
3	-7	1	12.8	13.3
-4	7	1	11.0	11.2
4	-7	1	36.5	36.6
-5	7	1	42.8	43.1
5	-7	1	8.9	-8.9
-6	7	1	12.2	-11.3
6	-7	1	19.3	-19.1
-7	7	1	15.5	-15.7
7	-7	1	4.4	3.6
0	0	2	57.4	-51.9
1	0	2	16.0	16.1
-1	0	2	36.6	36.0
2	0	2	44.2	-42.4
-2	0	2	13.5	13.2
3	0	2	60.0	-61.1
-3	0	2	16.5	-16.9
4	0	2	12.4	-12.2
-4	0	2	7.2	-7.4
5	0	2	61.2	61.5
-5	0	2	29.7	-30.8
6	0	2	12.2	11.3
-6	0	2	5.5	-6.5
-7	0	2	14.0	14.2
0	1	2	45.6	45.0
0	-1	2	57.4	-58.3
1	1	2	49.3	50.5
-1	1	2	52.7	-52.2
1	-1	2	41.3	40.0
1	1	-2	53.6	-52.7
2	1	2	18.9	-18.7
-2	1	2	45.9	-44.7
2	-1	2	42.0	42.7
2	1	-2	4.8	5.8
3	1	2	14.8	-14.6
-3	1	2*	0.9	-0.6
3	-1	2	19.2	-18.7
3	1	-2	19.0	18.6
4	1	2	9.4	-10.2
-4	1	2	22.5	22.5
4	-1	2	34.0	-33.9
4	1	-2	36.3	-36.6
5	1	2	10.0	9.3
-5	1	2	8.7	-8.4
5	-1	2*	0.0	1.7
5	1	-2	5.8	-5.4
6	1	2*	3.4	-2.7
-6	1	2	12.7	-12.6
6	-1	2	9.0	8.7
6	1	-2	22.4	22.0
-7	1	2	6.8	6.2
7	-1	2	17.4	-17.6
0	2	2	18.1	19.2
0	-2	2	85.8	-87.2
1	2	2	7.9	7.5
-1	2	2	21.7	21.5
1	-2	2	14.0	14.5
1	2	-2	9.2	9.1
2	2	2	7.5	8.3
-2	2	2	75.9	-75.9
2	-2	2*	0.6	4.3
2	2	-2	77.4	77.9
3	2	2	4.1	4.0
-3	2	2	7.7	6.9
3	-2	2	12.6	-12.6
3	2	-2	12.2	-12.6
4	2	2	12.1	-11.4
-4	2	2	66.7	68.0
4	-2	2	4.5	-4.2
4	2	-2	31.8	-30.8
5	2	2	7.8	7.8
-5	2	2*	2.4	-1.1
5	-2	2	22.4	23.5
5	2	-2	5.6	4.5
-6	2	2	22.9	-22.0
6	-2	2	14.5	-14.3
6	2	-2	5.8	5.9
-7	2	2*	1.8	2.3
7	-2	2	6.1	-5.3
0	3	2	5.4	-6.1
0	-3	2	6.7	6.1
1	3	2	15.0	15.8
-1	3	2*	0.0	0.9
1	-3	2	44.8	43.7
1	3	-2	10.9	9.5
2	3	2	24.7	-25.5
-2	3	2	48.6	47.5
2	-3	2	3.0	-1.8
2	3	-2	18.5	-19.4
3	3	2	13.5	14.3
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3	-3	2	13.6	-13.3
3	3	-2	5.7	5.5
4	3	2	20.3	20.2
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4	-3	2	7.9	-7.4
4	3	-2*	2.7	-4.2
-5	3	2	12.6	-13.1
5	-3	2*	2.9	1.8
5	3	-2*	3.4	4.5
-6	3	2	9.2	9.5
6	-3	2	13.6	13.5
-7	3	2*	0.0	-0.2
7	-3	2	3.4	0.6
0	4	2	49.4	51.2
0	-4	2*	3.7	3.9
1	4	2	8.2	8.6
-1	4	2	18.0	-17.8
1	-4	2	42.4	41.7
1	4	-2	28.2	-27.5
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2	-4	2	17.1	-17.3
2	4	-2	20.9	20.6
3	4	2	8.9	8.2
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3	-4	2	6.9	-7.0
3	4	-2	20.9	20.9
-4	4	2*	2.9	-0.3
4	-4	2	45.2	45.0
4	4	-2	17.1	-16.0
-5	4	2	38.2	-37.5
5	-4	2	8.9	9.7
-6	4	2	28.2	29.0
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-7	4	2	22.3	22.4
7	-4	2	9.2	9.7
0	5	2	3.8	3.8
0	-5	2*	0.7	1.1
1	5	2	33.8	34.9
-1	5	2	14.6	-14.9
1	-5	2	11.3	11.3
1	5	-2	15.8	16.7
2	5	2	6.1	-6.4
-2	5	2	26.0	-26.4
2	-5	2	20.3	-20.3
2	5	-2	10.0	10.0
-3	5	2	5.8	-5.8
3	-5	2	7.1	-6.5
3	5	-2	9.9	10.0
-4	5	2	25.9	25.9
4	-5	2	3.9	4.8
-5	5	2*	0.7	1.8
5	-5	2	24.8	24.9
-6	5	2	11.1	11.4
6	-5	2	10.4	10.8
-7	5	2	3.9	3.6
7	-5	2	15.2	-15.2
0	6	2	13.8	14.3
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1	6	2	24.8	25.0
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1	-6	2*	1.9	1.7
1	6	-2	21.0	-22.6
-2	6	2	6.8	6.6
2	-6	2	10.4	9.9
2	6	-2	9.7	8.8
-3	6	2	26.0	25.8
3	-6	2	27.1	27.5
-4	6	2*	1.9	0.2
4	-6	2	4.0	3.7
-5	6	2	19.1	-19.6
5	-6	2	37.1	-36.7
-6	6	2	9.3	-9.7
6	-6	2	14.8	15.3
-7	6	2	23.6	-23.2
7	-6	2	16.4	16.3
0	7	2	8.1	7.1
0	-7	2	20.7	-21.2
-1	7	2	8.8	-8.9
1	-7	2	13.8	-13.5
1	7	-2	13.8	14.5
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2	-7	2	22.5	22.5
-3	7	2	8.1	-8.4
3	-7	2	15.4	13.3
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4	-7	2	26.3	-26.5
-5	7	2	10.4	10.4
5	-7	2	22.2	-21.4
-6	7	2	10.6	-11.3
6	-7	2*	0.0	1.4
-7	7	2	22.3	-22.7
7	-7	2	14.4	14.3
0	0	3	4.5	4.0
1	0	3	17.3	16.4
-1	0	3	9.1	8.0
2	0	3*	2.7	-0.2
-2	0	3	7.1	7.0
3	0	3	3.4	2.3
-3	0	3	6.0	-6.5
4	0	3*	2.7	0.2
-4	0	3	6.5	-7.1
5	0	3	8.4	8.9
-5	0	3	12.1	13.4
6	0	3*	0.0	0.0
-6	0	3	9.7	9.6
-7	0	3*	4.0	-4.9
0	1	3	47.0	-50.4
0	-1	3	22.2	-21.2
1	1	3	12.0	-12.3
-1	1	3	36.7	35.7
1	-1	3	64.0	65.2
1	1	-3	7.8	-9.6
2	1	3	28.3	28.8
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2	-1	3*	2.0	2.9
2	1	-3	27.2	-25.7
3	1	3	5.7	4.3
-3	1	3	34.0	33.0
3	-1	3	42.8	-44.2
3	1	-3	5.1	-5.7
4	1	3	12.3	13.1
-4	1	3	12.4	-12.3
4	-1	3	7.6	7.5
4	1	-3	9.7	-8.4
5	1	3*	3.4	3.9
-5	1	3	15.1	14.8
5	-1	3*	0.0	1.8
5	1	-3	21.3	21.4
-6	1	3	14.0	-14.8
6	-1	3*	3.3	-3.3
6	1	-3	4.6	4.5
-7	1	3	6.9	-6.6
0	2	3	27.3	26.3
0	-2	3	16.4	14.0
1	2	3	17.2	17.6
-1	2	3	46.3	45.0
1	-2	3	48.8	-48.0
1	2	-3	16.3	15.7
2	2	3	3.9	3.3
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2	-2	3	30.2	-29.0
2	2	-3*	3.1	3.3
3	2	3	9.0	9.3
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3	-2	3	14.8	-14.4
3	2	-3	20.4	20.3
4	2	3	24.3	-24.6
-4	2	3	9.5	-10.2
4	-2	3	3.7	3.0
4	2	-3	35.4	-35.5
5	2	3*	3.5	-3.9
-5	2	3*	0.0	0.6
5	-2	3	5.9	5.4
5	2	-3	31.6	-31.5
-6	2	3	38.5	38.0
6	-2	3	6.3	6.2
6	2	-3	9.9	9.0
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7	-2	3	10.1	-9.3
0	3	3	24.7	-24.9
0	-3	3	26.0	-25.5
1	3	3	13.8	-14.0
-1	3	3	24.4	24.0
1	-3	3*	0.0	1.4
1	3	-3	34.7	-33.6
2	3	3	22.8	23.4
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2	-3	3	37.6	-36.9
2	3	-3	24.9	24.8
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-3	3	3*	1.5	2.3
3	-3	3	25.9	25.8
3	3	-3	20.7	20.0
4	3	3	20.2	-20.4
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4	-3	3	24.9	25.5
4	3	-3	40.4	-39.6
-5	3	3	14.8	-14.5
5	-3	3	36.6	-36.8
5	3	-3	7.2	-6.7
-6	3	3	31.2	-31.8
6	-3	3*	0.0	-0.9
-7	3	3	31.4	31.9
7	-3	3	13.1	13.9
0	4	3	16.2	16.4
0	-4	3	27.9	-28.0
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2	4	-3*	0.0	-1.0
3	4	3	22.9	-22.5
-3	4	3	34.4	33.9
3	-4	3	17.6	17.6
3	4	-3	12.4	-12.5
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4	4	-3	9.1	-8.4
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6	-4	3*	0.0	1.2
-7	4	3	4.0	-3.0
7	-4	3	25.9	25.2
0	5	3	35.3	35.9
0	-5	3	39.9	40.6
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1	5	-3	23.2	24.0
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2	-5	3	24.0	-24.0
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3	-5	3	59.3	60.3
3	5	-3*	2.4	1.2
-4	5	3	40.3	40.9
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7	-5	3	17.7	17.6
0	6	3*	0.0	-1.3
0	-6	3	17.0	17.2
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1	-6	3	3.5	3.4
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-3	6	3*	2.0	2.8
3	-6	3	4.1	4.8
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5	-6	3	13.6	-13.4
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6	-6	3	3.3	3.0
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7	-6	3	13.6	13.8
0	7	3	15.4	14.7
0	-7	3*	2.9	0.5
-1	7	3	5.2	-5.0
1	-7	3	30.6	-29.7
1	7	-3	18.0	18.0
-2	7	3	9.6	-9.5
2	-7	3	19.0	18.5
-3	7	3	10.0	9.8
3	-7	3	20.3	19.9
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4	-7	3	3.4	2.5
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5	-7	3*	2.8	-1.8
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6	-7	3	4.0	3.1
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7	-7	3	16.6	-16.5
0	0	4	20.9	-21.9
1	0	4	31.2	-29.8
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4	0	4	18.0	18.1
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0	1	4	44.0	-44.0
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1	-1	4	33.2	-32.3
1	1	-4	52.2	51.3
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2	1	-4	19.3	19.3
3	1	4	26.4	-27.0
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3	-1	4	29.3	30.0
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4	1	4	19.9	-19.8
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4	1	-4	6.1	-5.9
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5	-1	4	19.9	-19.6
5	1	-4	7.4	7.3
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2	2	-4	7.0	-6.6
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3	2	-4	33.7	33.7
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5	-2	4	46.8	-46.7
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6	-2	4	9.0	-8.9
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0	3	4	14.8	-14.7
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3	3	4	6.9	6.7
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3	-3	4	30.1	-30.2
3	3	-4	38.3	-38.3
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-4	3	4	10.2	-10.8
4	-3	4	3.5	-1.6
4	3	-4*	1.8	0.7
-5	3	4	3.5	-3.4
5	-3	4	12.8	13.4
5	3	-4	17.6	17.6
-6	3	4	18.6	-18.9
6	-3	4	3.8	-2.6
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7	-3	4	4.5	4.6
0	4	4	40.2	-40.8
0	-4	4	8.2	7.3
1	4	4	20.2	-20.6
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1	-4	4	53.6	-54.0
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2	4	4	22.7	22.3
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2	-4	4	7.4	7.7
2	4	-4	24.0	-23.2
3	4	4*	2.5	-2.0
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3	-4	4	34.8	35.9
3	4	-4	6.2	-6.6
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4	4	-4	9.5	8.7
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6	-4	4	25.8	26.3
-7	4	4	12.1	-12.3
7	-4	4	13.7	-12.7
0	5	4	10.2	10.5
0	-5	4	21.5	-21.5
1	5	4*	2.2	-1.4
-1	5	4	12.8	13.6
1	-5	4	49.2	-50.5
1	5	-4	14.6	14.9
2	5	4	5.3	4.9
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2	-5	4*	2.2	-1.9
2	5	-4	25.5	24.9
-3	5	4	15.8	-16.2
3	-5	4	18.4	19.0
3	5	-4	7.4	-7.0
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4	-5	4	19.6	20.4
-5	5	4	13.3	13.7
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6	-5	4	4.7	-5.4
-7	5	4	14.6	15.2
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0	6	4	10.3	-10.4
0	-6	4	11.6	-11.2
-1	6	4*	2.8	-3.4
1	-6	4	20.8	-20.9
1	6	-4	20.6	21.0
-2	6	4	19.7	-19.6
2	-6	4	38.2	38.7
2	6	-4*	0.0	-3.1
-3	6	4	33.5	33.7
3	-6	4	12.4	12.9
-4	6	4	30.6	31.0
4	-6	4	31.1	-31.8
-5	6	4	14.9	-14.8
5	-6	4	9.6	-9.6
-6	6	4	9.6	-9.8
6	-6	4	8.5	-7.5
-7	6	4	19.2	19.9
7	-6	4*	0.2	2.3
0	-7	4	4.6	5.2
-1	7	4	17.4	-16.9
1	-7	4	14.2	-14.1
-2	7	4*	2.0	-3.2
2	-7	4	6.1	-6.8
-3	7	4	19.3	19.4
3	-7	4	8.2	7.5
-4	7	4	7.7	8.3
4	-7	4	14.3	14.0
-5	7	4	9.0	-8.5
5	-7	4	5.3	-4.9
-6	7	4	6.3	-6.8
6	-7	4*	3.3	-4.4
-7	7	4	14.8	15.5
0	0	5	7.0	7.4
1	0	5*	0.0	-1.4
-1	0	5*	0.0	0.8
2	0	5	16.3	-16.2
-2	0	5	5.2	-5.5
3	0	5	20.4	-21.1
-3	0	5	7.8	-7.7
4	0	5	15.1	14.5
-4	0	5	8.2	-8.3
5	0	5*	1.5	1.1
-5	0	5	10.0	-10.4
-6	0	5*	0.0	-0.7
0	1	5	8.6	7.7
0	-1	5	37.4	39.0
1	1	5	3.1	3.2
-1	1	5	70.1	-70.2
1	-1	5	18.3	-17.9
1	1	-5	11.0	-10.6
2	1	5	21.9	-22.5
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2	-1	5	14.1	-14.0
2	1	-5	16.7	-16.9
3	1	5	21.6	21.1
-3	1	5	17.1	17.3
3	-1	5	7.2	7.2
3	1	-5*	0.0	-1.8
4	1	5	20.1	19.8
-4	1	5*	0.0	0.4
4	-1	5	12.4	-12.8
4	1	-5	8.8	-9.7
-5	1	5*	0.0	1.2
5	-1	5	8.2	-8.4
5	1	-5	9.8	-9.9
-6	1	5	10.1	10.8
6	1	-5	22.4	22.6
-7	1	5	22.9	-22.9
0	2	5	11.6	11.7
0	-2	5	26.1	-26.1
1	2	5	42.6	-43.2
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1	-2	5	35.5	-35.9
1	2	-5	27.2	27.2
2	2	5	9.4	-9.5
-2	2	5	25.9	25.7
2	-2	5*	2.5	-2.3
2	2	-5	44.2	44.7
3	2	5*	2.4	-4.1
-3	2	5	30.2	-30.3
3	-2	5	40.1	39.5
3	2	-5	14.7	-15.1
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-4	2	5	42.4	-43.5
4	-2	5	20.7	20.6
4	2	-5*	2.9	-3.0
-5	2	5	5.1	5.1
5	-2	5	11.0	-10.4
5	2	-5	7.5	8.4
-6	2	5	11.1	11.8
6	-2	5	9.2	-8.6
-7	2	5*	2.4	-0.4
0	3	5	30.7	-30.8
0	-3	5	31.1	30.8
1	3	5	10.9	11.2
-1	3	5*	1.8	1.3
1	-3	5	52.9	-54.0
1	3	-5	56.6	56.6
2	3	5	14.4	14.4
-2	3	5	51.0	50.4
2	-3	5	14.5	14.8
2	3	-5	19.6	-20.6
3	3	5*	0.0	-1.9
-3	3	5	25.6	-25.4
3	-3	5	37.2	36.9
3	3	-5	29.6	-28.7
-4	3	5	49.4	-49.7
4	-3	5*	1.9	-3.2
4	3	-5	17.6	17.4
-5	3	5	33.7	34.6
5	-3	5	11.2	-11.7
5	3	-5	10.6	10.6
-6	3	5	41.9	42.2
6	-3	5*	1.5	0.2
-7	3	5	21.2	-22.0
0	4	5	6.3	-6.5
0	-4	5	21.4	21.8
1	4	5	10.1	9.2
-1	4	5	11.1	-11.6
1	-4	5*	0.0	-1.4
1	4	-5	13.7	-13.5
2	4	5	28.4	28.0
-2	4	5	23.5	24.1
2	-4	5	19.0	-19.2
2	4	-5*	0.0	0.0
-3	4	5*	0.2	0.1
3	-4	5	17.4	17.8
3	4	-5	4.5	-3.0
-4	4	5	12.6	-13.1
4	-4	5	19.2	19.6
4	4	-5	18.8	18.8
-5	4	5	17.1	17.0
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-6	4	5	23.8	24.0
6	-4	5	19.6	-19.6
-7	4	5*	1.0	1.2
0	5	5	18.6	-19.1
0	-5	5	6.2	-6.1
1	5	5	14.9	14.8
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1	-5	5	14.0	14.8
1	5	-5	7.3	8.1
-2	5	5	26.6	26.8
2	-5	5*	0.0	2.7
2	5	-5	6.4	-6.2
-3	5	5	9.1	8.7
3	-5	5	29.5	-29.4
3	5	-5	17.1	-18.1
-4	5	5	12.5	-12.5
4	-5	5	8.0	8.5
-5	5	5	7.4	8.1
5	-5	5	32.6	32.3
-6	5	5	4.7	-5.0
6	-5	5	26.3	-25.4
-7	5	5	11.5	11.0
0	6	5	7.1	7.5
0	-6	5	7.8	8.5
-1	6	5	6.2	-5.7
1	-6	5*	0.0	1.2
1	6	-5	11.3	-11.5
-2	6	5	7.6	-7.4
2	-6	5	12.4	-11.7
-3	6	5	11.8	11.7
3	-6	5	20.6	-20.8
-4	6	5	11.2	11.9
4	-6	5*	0.0	0.2
-5	6	5	12.1	-12.8
5	-6	5	21.8	21.4
-6	6	5	7.3	-6.6
6	-6	5	5.4	-4.6
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0	-7	5	22.1	-21.2
1	-7	5	8.8	8.9
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2	-7	5*	1.3	-1.1
-3	7	5	21.8	-21.9
3	-7	5	4.4	-4.1
-4	7	5	7.0	7.0
4	-7	5	8.0	8.2
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5	-7	5*	2.9	1.5
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-7	7	5	10.7	11.0
0	0	6	36.5	37.6
1	0	6	73.7	-74.2
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2	0	6	33.2	-34.1
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3	0	6	55.2	55.8
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4	0	6	3.6	-1.4
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0	1	6	5.9	4.9
0	-1	6	23.7	23.4
1	1	6	20.8	-20.9
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1	-1	6	18.0	-19.3
1	1	-6	6.8	-6.6
2	1	6*	1.6	1.5
-2	1	6	9.2	9.9
2	-1	6	41.3	-41.8
2	1	-6	34.3	-34.5
3	1	6	17.0	16.3
-3	1	6	38.8	-40.6
3	-1	6	13.7	14.6
3	1	-6*	3.3	0.7
4	1	6	5.3	6.0
-4	1	6	6.2	6.5
4	-1	6	26.5	27.2
4	1	-6	25.1	25.6
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5	-1	6	15.6	-15.1
5	1	-6	4.3	4.9
-6	1	6*	1.6	0.7
6	1	-6	22.6	-23.0
-7	1	6	11.2	-11.6
0	2	6	36.2	36.1
0	-2	6*	0.0	2.5
1	2	6	5.7	6.1
-1	2	6*	1.9	-0.6
1	-2	6	3.2	3.4
1	2	-6	3.6	-3.5
2	2	6	23.1	-23.6
-2	2	6	5.7	-5.2
2	-2	6	12.8	13.0
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3	2	6	12.7	13.4
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3	-2	6	8.1	-7.9
3	2	-6	25.8	-25.9
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4	-2	6	21.3	-21.9
4	2	-6	35.3	34.1
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5	-2	6	15.7	15.7
5	2	-6*	2.2	0.1
-6	2	6	48.9	49.0
-7	2	6*	0.9	-1.8
0	3	6	6.8	7.1
0	-3	6	3.8	3.2
1	3	6	3.7	2.2
-1	3	6	9.2	-9.1
1	-3	6	4.5	-4.7
1	3	-6	18.5	19.8
2	3	6*	1.9	-1.3
-2	3	6	10.8	9.6
2	-3	6	25.1	-25.5
2	3	-6	5.4	4.9
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3	-3	6	3.6	-2.2
3	3	-6	8.1	-8.4
-4	3	6	23.5	23.9
4	-3	6*	0.8	0.2
4	3	-6	6.0	-5.1
-5	3	6	18.0	-18.7
5	-3	6	15.6	15.7
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0	4	6	14.5	14.2
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1	4	6*	1.9	4.1
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1	-4	6	4.4	-2.2
1	4	-6	15.6	16.1
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2	-4	6	14.5	14.0
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-3	4	6	8.2	-8.4
3	-4	6*	3.3	-3.5
3	4	-6	14.9	-14.6
-4	4	6	4.1	-3.4
4	-4	6*	2.5	4.1
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1	5	-6	3.8	-3.0
-2	5	6	20.3	20.0
2	-5	6	12.1	-11.9
2	5	-6*	3.1	0.6
-3	5	6	32.2	-31.9
3	-5	6	33.9	35.1
-4	5	6	12.9	-12.9
4	-5	6	17.3	17.3
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-6	5	6*	3.1	4.0
6	-5	6	21.1	-20.8
-7	5	6	15.4	-14.8
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3	-6	6	25.2	-25.2
-4	6	6	19.6	-19.3
4	-6	6	25.4	25.7
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1	-7	6	10.1	9.4
2	-7	6*	2.6	-3.9
-3	7	6	3.9	-3.3
3	-7	6*	0.0	-3.0
-4	7	6*	0.0	-1.8
4	-7	6*	1.6	1.0
-5	7	6	4.3	-4.8
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0	0	7	5.0	6.0
1	0	7*	0.0	-0.7
-1	0	7	3.8	-1.7
2	0	7	6.9	-7.9
-2	0	7	14.7	15.1
3	0	7	14.0	13.7
-3	0	7	10.5	10.5
4	0	7	3.7	2.2
-4	0	7*	0.0	-3.6
-5	0	7	4.3	2.2
-6	0	7	5.1	5.4
0	1	7	15.3	16.0
0	-1	7	24.9	-25.6
1	1	7	3.6	-1.6
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1	-1	7	5.5	5.8
1	1	-7	49.5	50.9
2	1	7	17.3	17.4
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2	-1	7	7.3	7.2
2	1	-7	15.6	16.1
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3	-1	7	15.4	-15.9
3	1	-7	48.4	-48.8
-4	1	7	45.3	45.
4	-1	7	4.2	-4.
4	1	-7*	2.9	-2.
-5	1	7	6.9	-6.
5	1	-7	26.1	26.
-6	1	7	16.3	-16.
0	2	7*	0.0	0.1
0	-2	7	10.6	-11.4
1	2	7	5.6	-5.5
-1	2	7	12.1	12.6
1	-2	7	19.4	-21.1
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2	-2	7	7.0	7.7
2	2	-7	9.8	-10.3
-3	2	7	11.7	-12.6
3	-2	7	14.8	14.9
3	2	-7*	0.5	-2.9
-4	2	7	21.1	21.5
4	-2	7*	1.4	1.5
4	2	-7*	2.1	3.4
-5	2	7	5.4	5.5
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5	2	-7	8.6	8.2
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0	3	7	30.8	30.8
0	-3	7	9.1	-8.8
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2	3	-7	10.9	11.0
-3	3	7	5.2	-5.5
3	-3	7	20.7	-20.3
3	3	-7*	0.0	1.5
-4	3	7	3.4	-0.7
4	-3	7	18.6	19.2
4	3	-7*	2.5	-0.6
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5	-3	7	16.4	15.9
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-7	3	7*	2.6	-3.9
0	4	7*	3.2	3.2
0	-4	7	5.1	-5.6
1	4	7*	3.3	-3.7
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1	-4	7	42.4	42.3
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2	-4	7*	3.1	3.5
2	4	-7	22.5	-22.0
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3	-4	7	27.1	-27.3
3	4	-7	23.4	23.6
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0	-5	7	10.5	-10.1
-1	5	7	8.8	-8.6
1	-5	7	22.5	22.5
1	5	-7	19.0	-19.0
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2	-5	7	5.8	-5.9
2	5	-7	26.6	25.4
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3	-5	7	21.5	-22.7
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4	-5	7	5.1	5.1
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5	-5	7	9.2	9.4
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-3	6	7*	0.0	-1.9
3	-6	7	12.2	12.2
-4	6	7	3.8	-4.0
4	-6	7	10.5	-10.5
-5	6	7	5.8	5.5
-6	6	7*	0.0	-0.0
0	0	8	26.4	-27.2
1	0	8	12.4	12.8
-1	0	8	5.8	-5.8
2	0	8*	0.0	2.4
-2	0	8	20.6	20.6
3	0	8	26.5	-25.7
-3	0	8	19.3	19.7
-4	0	8*	1.8	-1.7
-5	0	8*	2.0	-0.2
0	1	8	17.1	17.7
0	-1	8*	2.9	3.8
1	1	8*	3.0	1.9
-1	1	8	6.1	5.5
1	-1	8	30.5	30.6
1	1	-8	23.6	-24.4
2	1	8	22.5	-22.7
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2	-1	8	13.6	13.7
2	1	-8	6.7	-7.2
-3	1	8	4.9	-5.7
3	-1	8	17.2	-16.5
3	1	-8	19.2	18.9
-4	1	8	4.9	4.
4	1	-8*	2.2	3.3
-5	1	8*	2.5	-0.3
5	1	-8	7.9	-8.3
-6	1	8	5.0	-1.7
0	2	8*	0.0	2.9
0	-2	8	12.4	-12.4
1	2	8	21.2	-21.5
-1	2	8	33.7	33.6
1	-2	8	41.9	42.2
1	2	-8	22.2	-22.6
2	2	8*	2.8	-0.4
-2	2	8	15.6	-15.3
2	-2	8	3.8	-0.6
2	2	-8	23.2	23.4
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3	-2	8	23.0	-23.6
3	2	-8	27.2	27.1
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4	-2	8	9.5	10.5
4	2	-8	26.4	-26.1
-5	2	8	11.6	11.5
-6	2	8	16.8	-17.6
0	3	8	6.8	-6.5
0	-3	8	3.8	-4.3
1	3	8*	2.4	3.7
-1	3	8	12.2	-11.4
1	-3	8	6.1	-5.4
1	3	-8*	0.0	0.8
-2	3	8	12.7	-13.2
2	-3	8	3.7	4.3
2	3	-8	12.6	11.8
-3	3	8	16.3	15.7
3	-3	8*	0.0	-3.3
3	3	-8	11.7	11.5
-4	3	8	3.9	3.4
4	-3	8	11.6	11.4
-5	3	8	4.4	3.0
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0	-4	8	7.4	7.4
-1	4	8	8.0	7.3
1	-4	8	7.8	8.0
1	4	-8	17.6	-18.0
-2	4	8	22.3	-22.5
2	-4	8	20.1	-19.9
2	4	-8*	1.3	0.7
-3	4	8	7.4	7.5
3	-4	8	6.4	6.5
-4	4	8	14.3	14.6
4	-4	8	12.8	13.1
-5	4	8	28.1	-27.6
-6	4	8*	2.8	-0.3
0	-5	8	8.5	-7.4
1	-5	8*	2.0	1.9
1	5	-8	8.0	-7.8
-2	5	8*	3.3	-3.6
2	-5	8	10.4	9.5
-3	5	8	14.9	14.4
3	-5	8	5.8	-6.4
-4	5	8	5.6	5.7
-5	5	8*	1.9	0.2

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* *The reflections marked by an asterisk were considered as unobserved. The column heads are* h, k, l, F_{obs}, and F_{calc}.

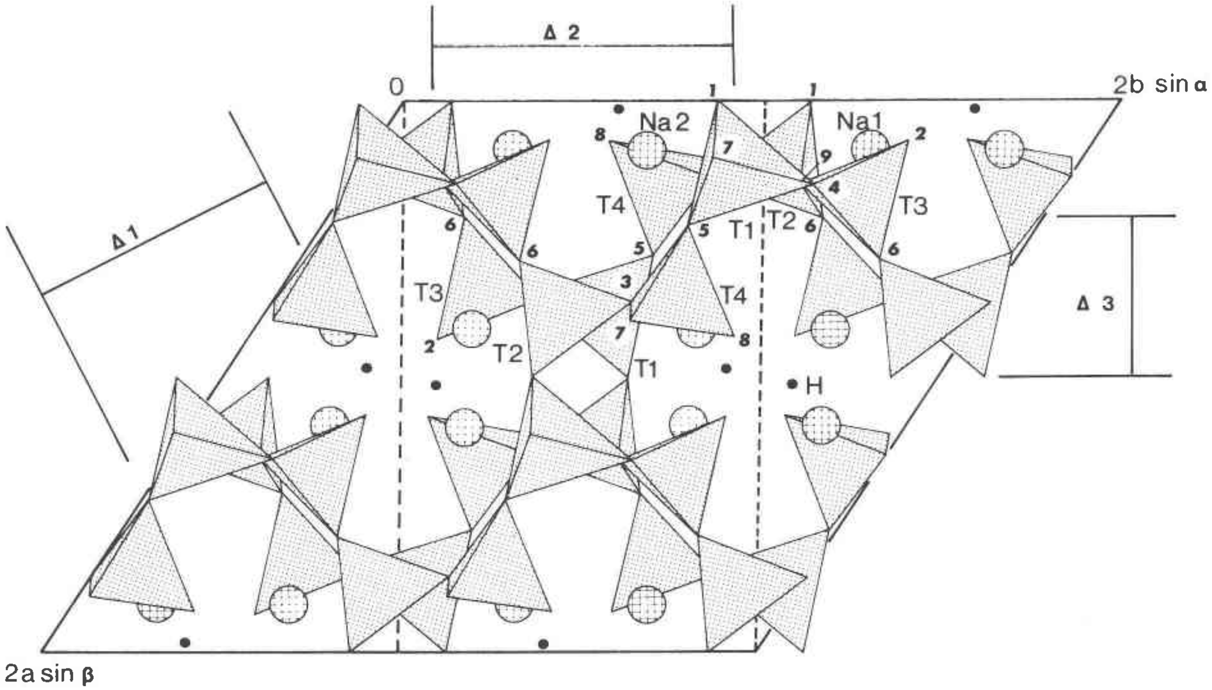

FIG. 1. The crystal structure of ussingite projected along [001]. The broken lines sketch the monoclinic pseudo-cell. Δ1, Δ2, Δ3 refer to the thickness of the partial projections shown in Figures 2, 3, and 4.

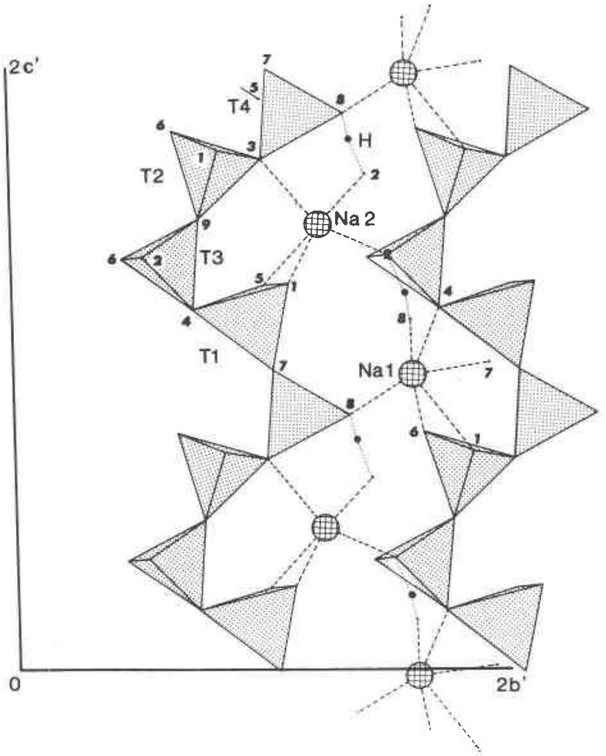

FIG. 2. Projection along [210] of a cell slab of thickness Δ3 (see Fig. 1); *b'* and *c'* are the projections of *b* and *c* onto the plane normal to [210].

lying around the centers at 0, 1/2, 0 and 0, 1/2, 1/2 are not bonded by bridging oxygen atoms, but through the sodium atoms and the short hydrogen bond between O(2) and O(8) (Figs. 1 and 2).

The type of framework described for ussingite was unknown until now. Bavenite (Cannillo, Coda, and Fagnani, 1966) and leifite (Coda, Ungaretti, and Della Giusta, 1974; formulas in Table 5) display interrupted frameworks of tetrahedra which are completely different from that of ussingite. The distinguishing structural features of ussingite compared with those of the mentioned silicates are summarized in Table 5 following Zoltai's (1960) classification.

The distribution of Si and Al in the four independent tetrahedra is apparently ordered. The mean *T*(1)–O bond length, 1.734 Å, indicates occupation of *T*(1) by aluminum. The remaining tetrahedral sites are mainly occupied by silicon according to the bond lengths shown in Table 3. The two non-bridging oxygen atoms O(2) and O(8) participate in *T*–O bonds whose lengths are quite different: the *T*(3)–O(2) distance (1.584 Å) is the shortest *T*–O bond while *T*(4)–O(8) (1.626 Å) is longer than average. This is explicable under the assumption that O(8) is the hydroxyl group.

The sodium atoms lie in cavities where the tetra-

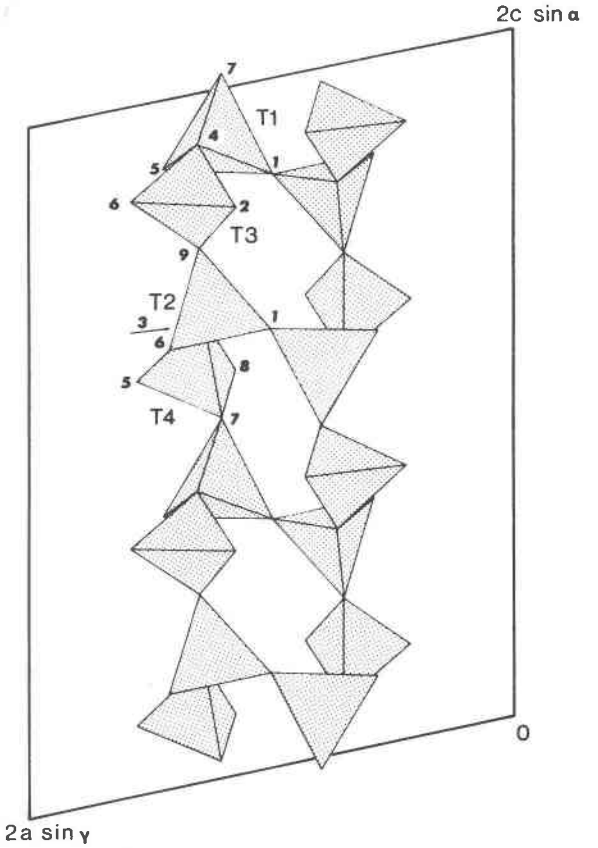

FIG. 3. Projection along [010] of a cell slab of thickness Δ2 (see Fig. 1).

hedral framework is interrupted (Fig. 1). Na(1) is surrounded by six oxygen atoms at distances ranging from 2.35 to 2.74 Å whereas Na(2) is linked to five oxygens with bond distances ranging from 2.28 to 2.52 Å (Fig. 2). The oxygen atoms are arranged around the two sodium atoms in irregular ways, so that it is difficult to describe the environment of these cations in terms of coordination polyhedra. The shortest sodium-sodium distance is 3.473 Å and occurs between two equivalent Na(2) atoms.

The balance of the electrostatic charges, computed with the method suggested by Donnay and Allmann (1970), is satisfactory, each oxygen atom receiving a sum of electrostatic bond strengths ranging from 1.84 to 2.14 valence units.

Ussingite displays a marked monoclinic pseudosymmetry. The parameters of the pseudo-monoclinic cell are: $a_m = 12.243$, $b_m = 7.686$, $c_m = 8.683$ Å, $\alpha_m = 90°45'$, $\beta_m = 102°4'$, $\gamma_m = 90°29'$. These values can be obtained from the parameters of the triclinic cell through the matrix (2 1 0/ 0 1 0/ 0 0 1).

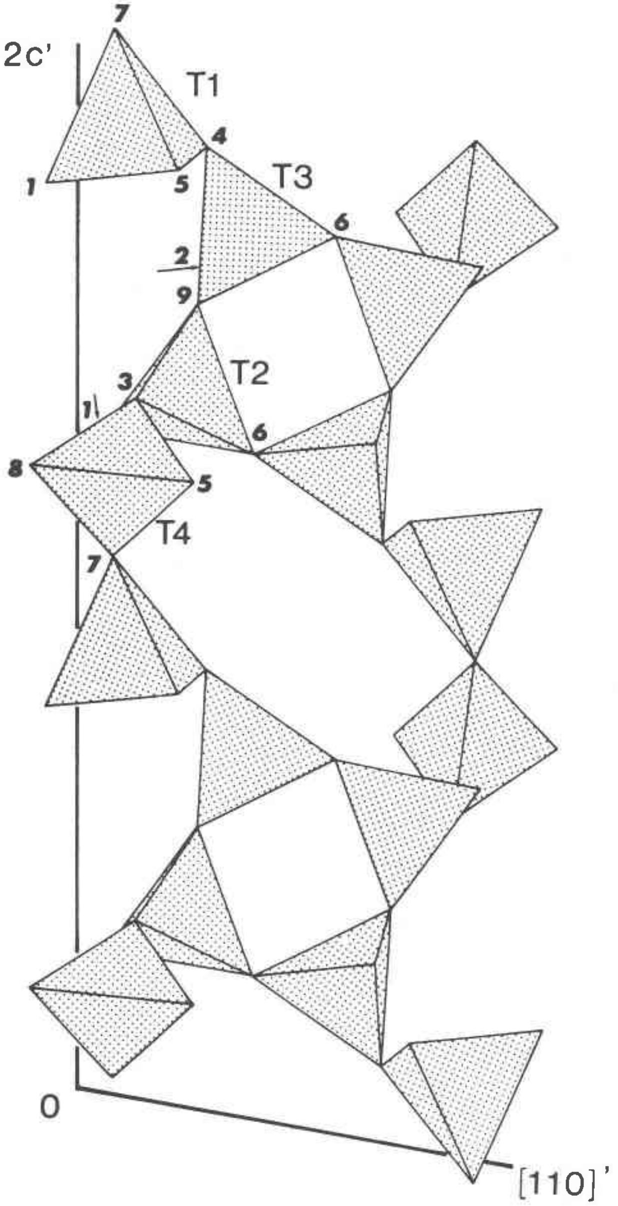

FIG. 4. Projection along [1$\bar{1}$0] of a cell slab of thickness Δ1 (see Fig. 1); c' and [110]' are the projections of c and [110] onto the plane normal to [1$\bar{1}$0].

TABLE 5. Comparison of Silicates with Interrupted Tetrahedral Framework Structures

Mineral	Chemical formula	Z	Sp. group	c *	n(f) **
Ussingite	$Na_2AlSi_3O_8OH$	2	$P\bar{1}$	1.875	4,6,8
Bavenite	$Ca_4Si_9Al_2(BeOH)_2O_{26}$	4	Cmcm	1.922	8(7),4(2)
Leifite	$Na_6Si_{16}Al_2(BeOH)_2O_{39}\cdot 1.5H_2O$	1	$P\bar{3}m1$	1.975	6(7),7(6), 5(6),4(3)

* Sharing coefficient (Zoltai, 1960). In framework silicates c = 2.

** n-membered loops of tetrahedra with their relative frequencies in parentheses. In ussingite the three loops of tetrahedra have the same frequency.

The $C2/c$ pseudo-symmetry is particularly evident in Figure 1 where the pseudo-monoclinic cell is outlined. The ordered distribution of Al and Si in the tetrahedra $T(1)$ and $T(2)$ and the asymmetric O(8)–H . . . O(2) hydrogen bond are the main structural features which account for triclinic symmetry. A hypothetical monoclinic ussingite would have a disordered Al-Si distribution in the tetrahedra now labelled $T(1)$ and $T(2)$; the non-equivalent oxygen atoms O(2) and O(8) would be equivalent and the O–H–O bond would be symmetric, or asymmetric with the two involved oxygen atoms acting statistically as donor and as acceptor.

Ussingite often shows lamellar twinning on $(\bar{1}20)$. This twin plane corresponds to the glide plane of the pseudo-monoclinic cell. Twinning could be explained on a structural basis assuming that, at the boundary between the two individuals of the twin, the pseudo-glide plane becomes a true glide plane, *i.e.*, both $T(1)$ and $T(2)$ are occupied by the same chemical species.

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