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Szaibelyite, $Mg_2(OH)[B_2O_4(OH)]$: Crystal Structure, Pseudosymmetry, and Polymorphism

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Abstract

Based on x- and y-coordinates determined by Peng, Wu, and Chang (1963), a complete structure has been established for szaibelyite (ascharite) and refined to $R = 5.9$ percent, using a crystal from Königshall-Hindenburg, Germany, twinned on (100): $P2_1/a$, a 12.577(2), b 10.393(2), c 3.139(1) Å, β 95.88(2)°, Z = 4[$Mg_2(OH)B_2O_4(OH)$], calculated density 2.738 g/cm³. Two non-equivalent chains of octahedra formed by oxygen atoms about magnesium are joined by sharing corners to form sheets parallel to (100). The sheets are held together by pyroborate groups, $B_2O_4(OH)$. Each octahedral chain has a strong twofold screw pseudosymmetry parallel to the c axis. The pseudosymmetry is such that the chain is nearly perfectly transformed by the screw operations into itself with average atomic displacement of only 0.056(4) Å. This situation theoretically permits generation of polymorphic variations of the structure. The cell dimensions and space groups of two simple variations are: (1) a 12.511, b 10.393, c 3.139 Å, $P2_12_12_1$; (2) a 25.022, b 10.393, c 3.139 Å, γ 90.00°, $P2_1/a$.

Introduction

Szaibelyite is a basic hydrous borate of magnesium, $MgHBO_3$, which was first described by Peters (1861). Other minerals having the same composition have also been described; for example, ascharite (Feit, 1891) and camsellite (Ellsworth and Poitevin, 1921). Though Winchell (1929) suggested from optical study that camsellite and szaibelyite might be different, there has been a generally accepted view that these three minerals are identical because they give similar X-ray powder diffraction patterns (Watanabe, 1939; Schaller, 1942).

The mineralogical confusion surrounding this mineral was principally due to its fibrous crystal habit which has hindered crystallo-chemical characterization. Based on crude fiber-rotation and Weissenberg photographs, the first single crystal data were proposed by Takéuchi (1957) for sussexite, the Mn analog of szaibelyite, from Mine Hill, Sussex County, New Jersey. With this information, the powder diffraction pattern of camsellite from British Columbia was indexed. An orthorhombic cell was proposed having the dimensions: a = 10.34 Å, b = 12.45 Å, c = 3.21 Å, and probable plane group pgg for the zero-level with c as rotation axis. Takéuchi (1958) further suggested the existence of pyroborate polyions in the structure of $MgHBO_3$ based on infrared absorption spectra, and proposed the formula $H_2Mg_2OB_2O_5$. Braitsch (1960) reported the following crystal data for ascharite from Stassfurt, Germany: a = 3.14 Å, b = 10.42 Å, c = 25.05 Å, and space group $B22_12$.

In contrast to these orthorhombic cells, Peng *et al* (1963) reported ascharite from north-eastern Kitai, China, to be monoclinic: a = 12.50 Å, b = 10.42 Å, c = 3.14 Å, β = 95°40′, and space group $P2_1/a$. Using $hk0$ reflections and the Patterson function, they carried out a two-dimensional structure analysis and showed that the structure does contain pyroborate groups in the form $[B_2O_4(OH)]$. Although their work elucidated the general structural scheme of ascharite, and a brief account of the structure has since appeared (Kudoh and Takéuchi, 1973), full details of the structure were needed in order to assess the different reported crystal data and to settle the confused status of natural $MgHBO_3$.

Experimental

Material from Königshall-Hindenburg in Reyershausen bei Göttingen was kindly placed at our disposal by the late Professor O. Braitsch, who described the material as ascharite. Higher-level Weissenberg photographs about the fiber axis invariably exhibited an unusual pattern (Fig. 1) that was readily interpreted as due to twinning of monoclinic crystals across (100). Between strong reflections in Figure 1, diffuse streaks are observed along the festoons corresponding to lattice rows

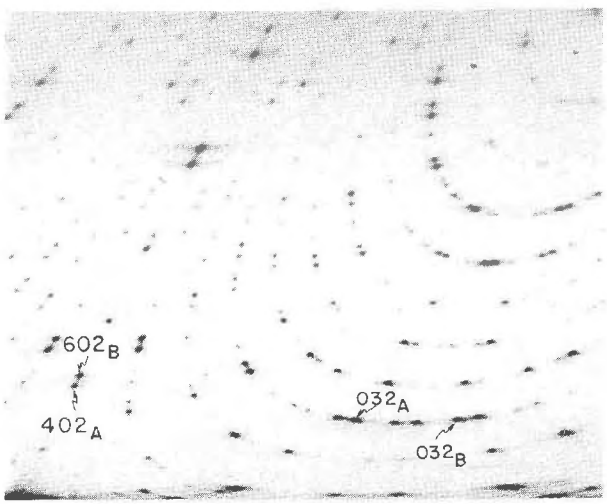

FIG. 1. Second level Weissenberg photograph (*c* axis rotation; Cu$K\alpha$ radiation), showing pairs of reflections due to twinning, and diffuse streaks. Indices of some of the reflections from twin individuals A and B are indicated.

parallel to the a^* axis, these indicating the existence of disorder in the structure. Some reflections in the photograph are also slightly diffuse along the horizontal line, showing that, to some extent, the crystal bears a fiber structure.

The unit cell data and intensities were collected from a twin composite having dimensions 0.10 × 0.15 × 0.30 mm along the a^*, b, and c axes, respectively. The cell dimensions obtained by single-crystal diffractometry (Cu $K\alpha_1$, λ = 1.540518 Å) are a = 12.577(2) Å, b = 10.393(2) Å, c = 3.139(1) Å, β = 95.88(2)°. Eight molecules of $MgHBO_3$ occur in this unit cell, the calculated density being 2.738 g/cm³. According to the survey made by Schaller (1942), observed densities for natural $MgHBO_3$ from various localities vary from 2.60 g/cm³ to 2.76 g/cm³. The space group is $P2_1/a$, $h0l$ and $0k0$ reflections being absent respectively when h and k are odd. The above crystal data agree with those reported by Peng *et al* (1963). We failed to find evidence for the B-centered orthorhombic crystal reported by Braitsch (1960).

A total of 699 independent reflections from one individual of the twin composite were then measured on a four-circle diffractometer up to sin θ = 0.906. The $hk0$ reflections are common to the individual crystals, so, to estimate the volume ratio, we compared intensities of several pairs of corresponding reflections from individual crystals. The ratio was found to be essentially unity; the intensities of $hk0$ reflections were therefore weighted by 0.5 with respect to those of other reflections. This scale factor for $hk0$ reflections was confirmed in the subsequent process of structure refinement.

Intensities of reflections thus measured were then corrected for Lorentz and polarization factors and reduced to structure factors. No absorption correction was made ($\mu_{CuK\alpha}$ = 49.2 cm^{-1}). Of the 699 reflections, those with intensities smaller than 2 σ (I) were excluded, and the remaining 466 reflections were used for structure determination.

Structure Determination

The x- and y-coordinates of atoms given by Peng *et al* (1963) were used as initial values for structure determination. Since the periodicity of the c axis is very short, approximate z coordinates of atoms were readily derived from the two-dimensional structure given by Peng *et al* (1963) by taking account of atomic distances and crystallo-chemical considerations. A Fourier map was then calculated using structure-factor signs based upon this initial set of atomic coordinates. In the map, the x- and y-coordinates of atoms reported by Peng *et al* (1963) were found to be essentially correct. After z-coordinates of atoms were slightly adjusted in the map, a calculation of structure factors yielded R = 20.6 percent.

The atomic parameters were refined by the full-matrix least-squares program, ORFLS, written for IBM 7090 computer by Busing, Martin, and Levy (1962) and modified by Iitaka for HITAC 5020E. For computations, an empirical weighting factor was used of the form: $w_i = 1/(a + F_0 + cF^2_0)$ (Cruickshank, 1965). The values a and c which minimized the variation of $(F_0 - F_c)$ with F_0 were 20 and 2/300 respectively. Cycles of refinement converged when the value of R was reduced to 5.9 percent for the set of 466 reflections.

Since it was anticipated that the hydrogen atoms might be located, a difference Fourier map was prepared at this final stage. The map indeed revealed two residual peaks; one is at the position x = 0.21, y = 0.39, z = 0.66 between O(4) (=OH) and O(2), and the other at the position x = 0.33, y = 0.28, z = 0.10 between O(6) (=OH) and O(3) (Fig. 2). After including hydrogen atoms at these positions, the value of R was reduced to 5.7 percent. The O(4)–H and O(6)–H bond lengths were found to be 0.80 Å and 1.02 Å respectively. Since, however, the O(6)–H ··· O(3) hydrogen bond is, as will be discussed later, weaker than the O(4)–H ··· O(2) hydrogen bond, the O(6)–H bond length should be smaller than O(4)–H length. Thus, the above coordi-

nates for hydrogen atoms are of uncertain accuracy. The atomic coordinates and thermal parameters are given in Table 1; the observed and calculated structure factors are compared in Table 2.

Description of Structure

Projected along the *c* axis, the structure is essentially the same as that reported by Peng *et al* (1963). The maximum difference in the *x*- and *y*-coordinates of atoms is found for the O(3) atom, the difference being 0.09 Å along the *a* axis. The structure (Fig. 2) contains distorted Mg–O octahedra which share edges to form a chain, two octahedra in width, parallel to the *c* axis. Two such non-equivalent chains, one a so-called *A* chain formed by Mg(1)–O octahedra and the other a *B* chain of Mg(2)–O octahedra, share corners (Fig. 2) to form a sheet parallel to (100).

The sheets are held together by pyroborate ions $[B_2O_4(OH)]^{3-}$. The pyroborate ion (Fig. 3) does not have all its oxygen atoms in a plane; instead, the directions of the normals to the two slanting triangles (one is BO_3 and the other BO_2OH) differ by 32.0(2)°. This feature of the pyroborate ion is in line with those of the pyroborate ions in $Co_2B_2O_5$ (Berger, 1950) and in $Mg_2B_2O_5$ (Takéuchi, 1952). However, compared to the B-O-B angle of 130.6(7)°, which is very close to that of 131.5° in $Mg_2B_2O_5$, the corresponding angle in $Co_2B_2O_5$ has a larger value of 153°. The B–O lengths and O–B–O angles are given in Tables 3 and 4, respectively.

TABLE 1. Atomic Parameters of Szaibelyite

Positional parameters

Atom	x	y	z	B(Å^2)
Mg(1)	0.5047(2)	0.1373(2)	0.2348(8)	0.80
Mg(2)	0.4129(2)	0.4208(2)	0.7104(8)	1.10
B(1)	0.1372(7)	0.1680(8)	0.7598(28)	1.42
B(2)	0.3072(7)	0.0472(8)	0.6253(30)	1.43
O(1)	0.0762(4)	0.0616(4)	0.7804(17)	1.24
O(2)	0.1012(4)	0.2908(5)	0.7750(17)	1.36
O(3)	0.2476(4)	0.1548(5)	0.7208(18)	1.68
O(4)	0.2481(4)	0.4485(4)	0.6078(18)	1.50
O(5)	0.4134(4)	0.0434(4)	0.7155(17)	1.27
O(6)	0.4084(4)	0.2953(5)	0.2059(18)	1.27

Anisotropic temperature factors (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg(1)	16(1)	13(2)	215(23)	1(2)	28(5)	2(6)
Mg(2)	21(1)	19(2)	297(24)	2(2)	24(5)	-14(7)
B(1)	28(6)	19(7)	383(94)	-10(6)	29(18)	10(22)
B(2)	30(6)	23(7)	372(88)	-5(5)	33(21)	14(22)
O(1)	26(3)	23(5)	302(54)	2(3)	24(11)	15(14)
O(2)	29(4)	22(5)	379(61)	-2(3)	26(13)	1(14)
O(3)	31(4)	30(5)	450(61)	-0(4)	16(13)	-18(15)
O(4)	34(4)	25(5)	379(55)	-0(3)	19(13)	43(14)
O(5)	27(3)	21(5)	300(54)	-2(3)	15(12)	1(14)
O(6)	27(3)	20(5)	354(58)	-4(3)	20(12)	6(14)

The expression used for the anisotropic thermal parameters was

$$\exp\left\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right\}$$

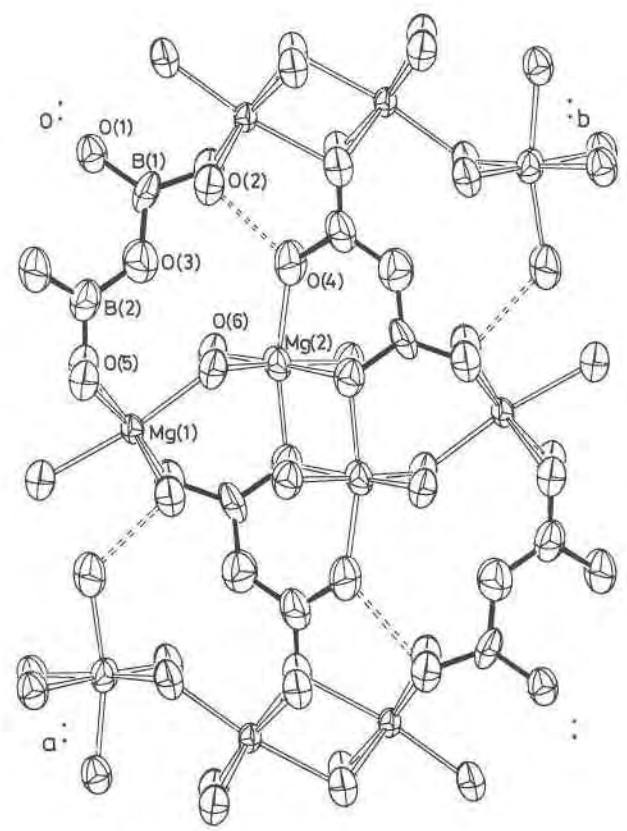

FIG. 2. The structure of szaibelyite projected on (001); thermal ellipsoids are shown. The B–O bonds are indicated by solid bars; hydrogen bonds by broken lines (a weak hydrogen bond between O(6)=OH and O(3) is not marked).

The hydroxl ion at O(4), which is associated with the pyroborate ion, forms a hydrogen bond with O(2) of another adjacent ion, the O(4)–O(2) distance being 2.564(7) Å. On the other hand, the hydroxyl ion at O(6), which is coordinated by three magnesium atoms, has a close anion neighbor, O(3), at the distance of 2.812(7) Å. This distance and the valence sums at O(6) and O(3) (Table 3) suggest the existence of a weak hydrogen bond between them. The valence sums were calculated using the techniques given by Donnay and Allmann (1970).

Pseudosymmetry and Polymorphism

In each octahedral chain, the octahedra are related to each other by inversion about the centers of symmetry which belong to the space group $P2_1/a$. Passing through the centers of symmetry and hence parallel to the chain axis, a strong pseudo 2_1 axis ex-

ists in the chain (Fig. 4). The operations of this pseudosymmetry combined with the inversion generate in the chain pseudo-mirror planes perpendicular to the chain axis and between the inversion centers. The situation is readily observed in Figure 5, which shows a view of the structure along the *b* axis. Since the octahedral chains are joined, as mentioned previously, to form sheets in the manner shown in Figure 4, the sheets themselves possess the same pseudosymmetry. The pseudosymmetry of the two-fold screw axis is such that the octahedral sheet is transformed by its operations nearly perfectly into itself with the average atomic displacement of only 0.056(4) Å along the *c* axis; the maximum displacement being 0.244(7) Å (Table 5).

The structure of szaibelyite can be divided into two unit slabs, each bounded by octahedral sheets (Fig. 5), that are related to each other by inversion about

TABLE 2. Observed and Calculated Structure Factors for Szaibelyite

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	2	0	63	69	9	2	0	33	29	-4	2	1	41	41	5	8	1	19	18	-4	7	2	12	9	8	2	2	23	22
0	4	0	63	61	9	3	0	38	36	-4	3	1	35	- 33	5	10	1	54	57	-4	8	2	42	42	8	3	2	20	19
0	6	0	27	25	9	4	0	76	74	-4	4	1	44	43	6	1	1	75	80	-4	9	2	27	26	8	4	2	28	28
0	8	0	91	96	9	6	0	20	20	-4	5	1	14	12	6	2	1	45	48	-3	1	2	25	23	8	6	2	22	21
0	10	0	70	67	9	7	0	29	27	-4	6	1	11	14	6	5	1	16	18	-3	2	2	50	51	9	1	2	19	20
0	12	0	34	33	9	8	0	49	50	-4	8	1	21	19	6	6	1	21	22	-3	3	2	50	51	9	2	2	18	20
1	2	0	13	20	10	0	0	106	96	-4	9	1	14	12	6	9	1	15	17	-3	4	2	44	44	9	4	2	14	15
1	3	0	41	34	10	1	0	50	47	-3	1	1	41	37	7	2	1	43	36	-3	7	2	47	46	10	1	2	15	13
1	4	0	16	17	10	3	0	27	28	-3	2	1	57	53	7	4	1	25	26	-3	8	2	44	41	10	2	2	14	11
1	5	0	31	32	10	4	0	19	15	-3	3	1	54	54	7	5	1	21	24	-2	0	2	139	142	11	2	2	22	20
1	6	0	45	45	10	6	0	28	25	-3	5	1	35	31	7	7	1	24	24	-2	2	2	31	31	11	3	2	29	26
1	7	0	114	114	11	1	0	12	10	-3	6	1	43	37	7	8	1	34	38	-2	3	2	48	44	-9	1	3	31	30
1	8	0	83	83	11	2	0	27	26	-3	9	1	24	23	7	10	1	30	30	-2	4	2	19	15	-9	2	3	12	11
1	9	0	24	24	11	3	0	36	33	-3	10	1	20	19	8	2	1	43	45	-2	5	2	49	45	-9	3	3	21	22
1	11	0	77	77	11	4	0	37	35	-3	11	1	34	33	8	3	1	33	29	-2	6	2	35	36	-8	1	3	13	16
2	0	0	89	93	11	5	0	20	21	-2	0	1	21	26	8	4	1	11	14	-2	7	2	16	11	-8	2	3	21	20
2	2	0	22	23	11	7	0	65	65	-2	1	1	61	56	8	6	1	19	20	-2	8	2	24	25	-8	3	3	49	53
2	3	0	76	85	12	2	0	28	27	-2	2	1	128	121	8	7	1	16	13	-2	10	2	11	10	-7	2	3	15	13
2	4	0	44	43	12	3	0	29	25	-2	3	1	20	22	8	9	1	12	16	-1	1	2	22	20	-7	4	3	58	61
2	5	0	71	70	12	4	0	35	36	-2	4	1	23	22	9	2	1	19	20	-1	2	2	12	13	-6	0	3	28	31
2	6	0	31	30	12	5	0	24	23	-2	5	1	104	103	9	3	1	39	40	-1	3	2	37	34	-6	1	3	36	38
2	8	0	19	24	12	6	0	16	18	-2	6	1	42	37	9	5	1	23	17	-1	5	2	25	21	-6	3	3	37	38
2	9	0	20	22	12	7	0	18	18	-2	9	1	56	55	9	6	1	56	56	-1	7	2	76	72	-6	4	3	19	21
2	10	0	12	14	13	1	0	15	12	-2	10	1	34	31	9	7	1	16	15	-1	8	2	18	16	-5	1	3	15	16
2	12	0	17	16	13	2	0	46	42	-1	1	1	28	23	10	0	1	16	20	-1	9	2	20	17	-5	2	3	22	24
3	1	0	38	36	13	3	0	20	20	-1	2	1	93	87	10	1	1	21	20	-1	10	2	14	13	-5	5	3	11	12
3	2	0	77	80	14	0	0	19	18	-1	4	1	88	85	10	3	1	13	15	0	0	2	189	194	-4	1	3	26	29
3	3	0	105	107	14	1	0	13	8	-1	6	1	70	71	10	5	1	60	60	0	1	2	43	35	-4	2	3	37	34
3	4	0	156	152	14	2	0	13	9	-1	7	1	39	35	11	2	1	30	31	0	3	2	48	45	-4	3	3	12	13
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3	7	0	72	75	-14	1	1	20	18	-1	10	1	34	32	12	0	1	25	25	0	7	2	22	19	-4	6	3	14	15
3	8	0	80	83	-14	2	1	20	23	0	0	1	47	44	12	3	1	24	24	0	8	2	23	22	-3	2	3	36	35
3	10	0	13	12	-13	2	1	39	44	0	1	1	71	69	12	5	1	36	34	0	10	2	16	19	-3	4	3	13	11
3	11	0	20	15	-13	4	1	21	23	0	2	1	65	55	-14	0	1	27	26	1	1	2	14	11	-3	5	3	12	12
4	1	0	28	29	-12	0	1	10	12	0	3	1	114	108	-13	1	2	14	13	1	3	2	18	17	-3	6	3	33	34
4	2	0	32	28	-12	3	1	40	39	0	5	1	109	113	-12	0	2	88	82	1	6	2	16	14	-3	7	3	15	14
4	3	0	29	25	-12	5	1	55	51	0	7	1	51	52	-12	1	2	21	15	1	7	2	37	36	-2	2	3	25	21
4	4	0	103	100	-11	2	1	21	19	0	8	1	19	19	-12	4	2	16	18	1	8	2	62	61	-2	3	3	44	43
4	5	0	11	13	-11	4	1	18	19	0	9	1	43	41	-11	1	2	22	21	1	9	2	12	11	-2	4	3	16	14
4	6	0	68	68	-11	6	1	58	53	0	10	1	23	18	-11	2	2	22	21	2	0	2	20	20	2	5	3	81	81
4	8	0	75	81	-10	1	1	27	29	0	11	1	40	39	-11	3	2	13	13	2	3	2	19	17	-2	7	3	18	17
4	9	0	27	31	-10	5	1	50	49	1	1	1	34	32	-11	5	2	13	9	2	4	2	26	26	-1	1	3	19	18
4	10	0	70	70	-9	3	1	50	52	1	2	1	80	71	-10	0	2	31	33	2	7	2	25	25	-1	2	3	46	41
5	1	0	131	129	-9	5	1	26	25	1	3	1	26	25	-10	1	2	29	31	2	8	2	22	22	-1	3	3	21	16
5	3	0	63	62	-9	6	1	25	28	1	4	1	27	26	-10	3	2	21	21	2	9	2	18	17	-1	4	3	39	35
5	4	0	21	23	-9	7	1	16	19	1	6	1	76	79	-9	1	2	18	16	3	1	2	35	36	-1	6	3	38	35
5	5	0	81	79	-9	8	1	30	28	1	7	1	28	29	-9	2	2	26	27	3	2	2	35	36	-1	7	3	15	12
5	6	0	20	17	-8	1	1	14	14	1	8	1	16	16	-9	3	2	39	39	3	3	2	57	58	0	0	3	11	12
5	8	0	17	17	-8	2	1	53	60	1	9	1	34	27	-9	4	2	22	20	3	4	2	16	18	0	2	3	33	33
5	9	0	20	22	-8	3	1	58	63	1	10	1	19	16	-9	5	2	14	12	3	5	2	20	22	0	5	3	30	24
5	10	0	11	9	-8	5	1	15	16	1	11	1	16	16	-9	6	2	12	13	3	7	2	22	25	0	6	3	12	13
6	0	0	222	217	-8	6	1	26	26	2	0	1	75	73	-9	7	2	16	13	3	8	2	25	28	1	2	3	39	41
6	2	0	64	61	-8	7	1	11	14	2	1	1	71	72	-8	2	2	40	42	4	0	2	42	45	1	5	3	22	22
6	3	0	28	28	-8	9	1	12	12	2	2	1	83	81	-8	3	2	35	39	4	1	2	22	22	1	6	3	26	25
6	4	0	62	62	-7	2	1	11	18	2	3	1	35	31	-8	4	2	38	39	4	3	2	25	26	2	0	3	25	27
6	6	0	77	83	-7	4	1	87	91	2	4	1	25	26	-8	6	2	55	55	4	4	2	39	43	2	1	3	25	27
6	7	0	15	15	-7	5	1	15	16	2	5	1	63	62	-8	8	2	44	46	4	6	2	43	47	2	2	3	29	29
6	8	0	114	121	-7	6	1	24	25	2	6	1	38	38	-7	1	2	68	71	4	8	2	56	60	2	3	3	16	16
7	1	0	74	76	-7	7	1	18	25	2	8	1	13	15	-7	5	2	38	41	5	1	2	63	65	2	5	3	34	34
7	2	0	27	27	-7	8	1	30	32	2	9	1	45	49	-7	6	2	29	29	5	2	2	25	25	2	6	3	23	25
7	3	0	56	56	-7	10	1	44	43	3	1	1	14	8	-7	7	2	23	23	5	3	2	18	19	3	1	3	15	14
7	4	0	31	30	-6	0	1	54	58	3	2	1	57	55	-7	8	2	29	29	5	6	2	15	15	3	3	3	14	12
7	5	0	62	63	-6	1	1	85	89	3	3	1	46	47	-6	0	2	64	67	5	7	2	15	13	3	4	3	28	27
7	6	0	72	73	-6	3	1	107	112	3	5	1	26	29	-6	1	2	19	18	6	0	2	46	48	3	5	3	12	12
7	8	0	57	61	-6	4	1	13	7	3	8	1	19	16	-6	4	2	27	29	6	1	2	11	11	4	1	3	35	35
7	9	0	12	10	-6	6	1	12	11	3	10	1	36	38	-6	6	2	36	36	6	2	2	22	25	4	3	3	47	50
8	0	0	76	69	6	9	1	12	13	3	11	1	18	19	-6	7	2	18	15	6	3	2	29	30	4	5	3	16	15
8	1	0	43	44	-5	2	1	38	43	4	0	1	28	27	-6	8	2	52	53	6	4	2	27	27	5	1	3	16	17
8	2	0	52	56	-5	3	1	31	31	4	1	1	47	49	-5	1	2	26	27	6	5	2	19	21	5	2	3	16	15
8	3	0	62	61	-5	4	1	63	63	4	2	1	44	45	-5	2	2	22	24	6	6	2	31	33	5	4	3	37	39
8	4	0	65	65	-5	5	1	17	17	4	3	1	57	58	-5	3	2	55	54	6	8	2	45	47	6	1	3	27	28
8	5	0	20	18	-5	7	1	28	26	4	4	1	47	49	-5	5	2	34	34	7	1	2	16	16	6	2	3	31	29
8	6	0	65	67	-5	8	1	22	21	4	6	1	13	11	-5	7	2	23	25	7	3	2	31	33	6	3	3	35	34
8	8	0	41	42	-5	10	1	53	54	4	7	1	18	18	-5	8	2	26	23	7	4	2	17	13	7	1	3	13	14
8	9	0	17	13	-5	11	1	18	17	5	2	1	16	15	-4	4	2	54	51	7	5	2	20	22	7	2	3	15	15
8	10	0	25	25	-4	0	1	31	31	5	4	1	105	110	-4	5	2	16	16	7	7	2	14	15					
9	1	0	41	39	-4	1	1	41	47	5	6	1	19	20	-4	6	2	24	24	8	0	2	48	52					

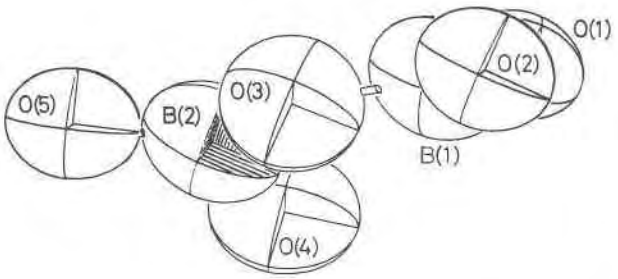

FIG. 3. The configuration of the pyroborate ion, $[B_2O_4OH]^{3-}$, viewed along the *b* axis.

the centers of symmetry in the sheets (Fig. 5). It is then possible, because of the pseudosymmetry, to derive a structure in which each unit slab is related to its adjacent slabs not by inversion but by twofold screw operations. Only very slight adjustments are required in the *z* coordinates of atoms in the octahedral sheets to achieve this structure. In this case, the twofold screw operations, whose axes are parallel to the *c* axis, may be regarded as stacking operations. The operations of this set of twofold screw axes and those of the original twofold screw axes parallel to the *b* axis in the unit slab form a group, generating in the new structure a third set of screw axes parallel to the direction corresponding to a^* of szaibelyite. The resulting structure therefore has space group $P2_12_12_1$.

TABLE 3. Bond Lengths and Valence Sums of Szaibelyite*

	Mg(1)	Mg(2)	B(1)	B(2)	Valence sum
O(1)		2.139 0.310	1.351 1.046		
		2.161 0.300			2.006
		2.051 0.349			
O(2)	2.118 0.336		1.357 1.034		
	2.115 0.338				1.708
O(3)			1.413 0.920	1.396 0.963	1.883
O(4) = OH		2.085 0.334		1.403 0.949	1.282
O(5)	2.214 0.292			1.337 1.088	
	2.132 0.330				2.037
	2.140 0.326				
O(6) = OH	2.037 0.377	2.048 0.350			
		2.035 0.357			1.084
Mean	2.126	2.088	1.373	1.379	

* Computed with the valence sum program provided by Prof. Gabrielle Donnay. Bond lengths (Å) are given in the first line of each pair, and bond valence (v.u.) in the second. Estimated errors in individual bond lengths are ±0.005 Å for Mg - O, and ±0.010 Å for B - O.

TABLE 4. O–O Distances and Bond Angles

Coordination group				Distance	Angle
B_2O_5 group	B(1) triangle	O(1)	O(2)	2.403	
			O(3)	2.388	
		O(2)	O(3)	2.341	
		O(1) - B(1) - O(2)			125.1(7)°
		O(1) - B(1) - O(3)			119.5(6)
		O(2) - B(1) - O(3)			115.4(8)
	B(2) triangle	O(3)	O(4)[s]	2.382	
			O(5)	2.387	
		O(5)	O(4)[s]	2.389	
		O(3) - B(2) - O(4)[s]			116.7(5)
		O(3) - B(2) - O(5)			121.7(5)
		O(5) - B(2) - O(4)[s]			121.3(5)
		B(1) - O(3) - B(2)			130.6(7)
		O(2) - O(3) - O(5)			171.0(2)
Mg(1) octahedron		O(6)	O(2)[g][c]	3.030	
			O(2)[g]	2.997	
			O(5)[c]	3.041	
			O(5)	3.065	
		O(2)[g]	O(2)[g][c]	3.139	
			O(5)[i]	3.039	
			O(5)	2.914	
		O(2)[g][c]	O(5)[c]	2.914	
			O(5)[i]	3.089	
		O(5)[c]	O(5)[i]	2.820	
			O(5)	3.139	
		O(5)[i]	O(5)	2.827	
Mg(2) octahedron		O(6)	O(6)[c]	3.139	
			O(1)[g]	3.023	
			O(4)	2.952	
			O(1)[s]	2.774	
		O(6)[c]	O(1)[g]	3.005	
			O(4)	3.058	
			O(1)[s][c]	2.774	
		O(1)[g]	O(1)[s]	2.779	
			O(1)[s][c]	2.785	
		O(4)	O(1)[s]	2.881	
			O(1)[s][c]	3.014	
		O(1)[s]	O(1)[s][c]	3.139	
		O(2)	O(4)[s]	2.564*	
		O(3)	O(6)	2.812	

Estimated errors in O - O distances are ± 0.007 Å.
* Hydrogen bond.

[s], [c], [g], [i] are code indicators showing coordinates of atoms equivalent by space group operation to the atoms at xyz. Corresponding operations are:
[s] twofold screw at 1/4, y, 1/2
[c] translation c
[g] glide a at x, 1/4, z
[i] inversion center at 1/2, 0, 1/2.
Two code indicators in sequence imply an atom related to the one at xyz by successive application of the two symbolized operations.

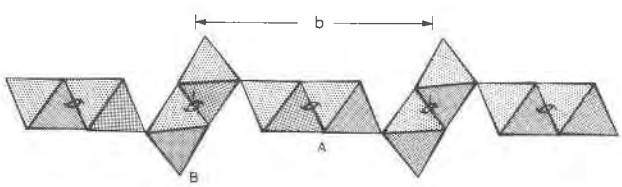

FIG. 4. The single octahedral sheet formed by *A* and *B* chains; projection along the *c* axis. Pseudosymmetry elements of 2_1 are indicated.

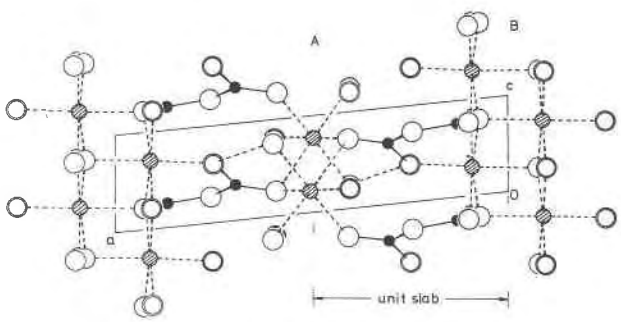

FIG. 5. The *b* axis projection of the structure bounded by $y = -¼$ and ¼ approximately. Solid circle: B, shaded circle: Mg, open circle: O, double open circle: OH.

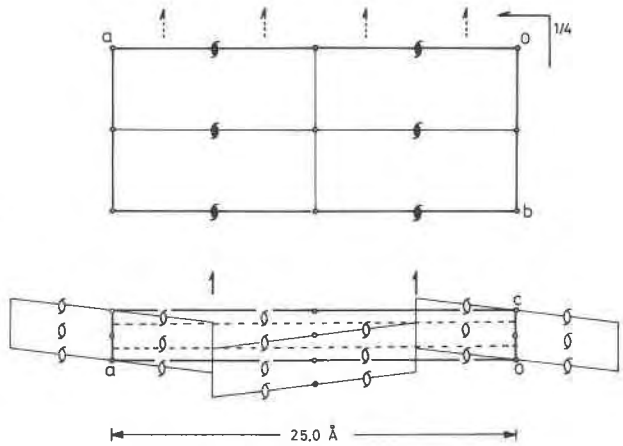

FIG. 6. The manner in which a twinned cell is formed of the monoclinic modification having a periodicity of 25 Å from the unit cells of szaibelyite; upper diagram shows the *c* axis projection, the lower diagram *b* axis projection. Note that this monoclinic modification has an orthogonal cell with its unique axis parallel to the *c* axis of szaibelyite. The twofold screw axes in szaibelyite remain in the twinned cell only as local symmetry; they are hence indicated in the upper diagram by dotted arrows, and in the lower by conventional notation but open style.

TABLE 5. Pseudosymmetry of Octahedral Chains

A-chain					
Coordinates of atoms in the Mg(1) octahedron					
	x	y	z		
Mg(1)	0.5047	0.1373	0.2348		
O(5)	0.4134	0.0434	0.7155	(2)	
O(5)'	0.5866	-0.0434	0.2845		
O(2)	0.6012	0.2092	0.7750	(2)	
O(6)	0.4084	0.2593	0.2059		
Coordinates of atoms in Mg(1)' octahedra					
	x'	y'	z'	Δz'(Å)	
Mg(1)'	0.4953	-0.1373	0.7652	0.049	
	0.4953	-0.1373	0.7809		
O(5)	0.4134	0.0434	0.7155		
O(5)'	0.5866	-0.0434	1.2845	0.007	(2)
	0.5866	-0.0434	1.2866		
O(2)'	0.3988	-0.2092	1.2250	0.103	(2)
	0.3988	-0.2092	1.1919		
O(6)'	0.5916	-0.2593	0.7941	0.041	
	0.5916	-0.2593	0.7811		
B-chain					
Coordinates of atoms in the Mg(2) octahedron					
	x	y	z		
Mg(2)	0.4129	0.4208	0.7104		
O(1)	0.4238	0.5616	0.2196	(2)	
O(6)	0.4084	0.2953	0.2059	(2)	
O(4)	0.2481	0.4485	0.6078		
O(1)'	0.5762	0.4384	0.7804		
Coordinates of atoms in Mg(2)' octahedra					
	x'	y'	z'	Δz'(Å)	
Mg(2)'	0.5871	0.5792	0.2896	0.024	
	0.5871	0.5792	0.2819		
O(1)	0.4238	0.5616	0.2196		
O(1)'	0.5762	0.4384	0.7804	0.005	(2)
	0.5762	0.4384	0.7822		
O(6)'	0.5916	0.7047	0.7941	0.041	(2)
	0.5916	0.7047	0.7811		
O(4)'	0.7519	0.5515	0.3922	0.244	
	0.7519	0.5515	0.3146		

The coordinates in the first line of each pair given for the atoms of Mg(1)' and Mg(2)' octahedra are for the case in which the atom is related to the corresponding atom in the Mg(1) or Mg(2) octahedron by inversion operation about the point at 1/2, 0, 1/2 of the space group $P2_1/a$, while those in the second line are for the case in which the atom is theoretically transformed from the corresponding atom by twofold screw operation about a hypothetical axis at 1/2, 0, z; the value of z' for the latter case is given by $1/2 + z + a(x' - x)\sin(\beta - 90)/c$. Numbers in brackets show the multiplicity of atoms.

In terms of Ito's (1950) theory on polymorphism, this orthorhombic structure may conveniently be described as a polysynthetic twin of szaibelyite taking place on the scale of a half unit cell.

Since it is conceivable that such a twin may occur on various scales of the unit slab (=half unit cell), we can theoretically derive various polymorphic (or polytypic) structures. Among possible polymorphic forms, one worth noting is the case in which twinnings take place on the scale of two unit slabs, namely, on the scale of a unit cell of szaibelyite. In this particular case, the twofold screw axes of unit slabs are located in the resulting orthogonal cell (Fig. 6). They do not form a group with the twinning (or stacking) operations. The twinning operations of the twofold screw axes form a group only with the inversion of the unit slab, generating a set of glide planes perpendicular to the *c* axis. Therefore, this polymorphic structure, despite its orthogonal cell, has a mono-

TABLE 6. Basic Polymorphic Forms of Szaibelyite

		Cell dimensions (Å)				Space group
		a	b	c		
1	monoclinic	12.577	10.393	3.139	β =95.88°	$P2_1/a$
2	orthorhombic	12.511	10.393	3.139		$P2_12_12_1$
3	monoclinic	25.022	10.393	3.139	γ =90.00	$P2_1/a$

Cell dimensions of the forms 2 and 3 were calculated from those of the present material given in the first line of this table.

clinic space group $P2_1/a$ with its new unique axis along the c axis of szaibelyite. Though this orthogonal cell has dimensions similar to those reported by Braitsch (1960) for his orthorhombic crystal, it obviously has different symmetry. So far as our study was concerned, it was not possible to derive the B-centered orthorhombic modification from the szaibelyite structure.

If the 'twinning' takes place in a random fashion, the resulting structure will evidently give a diffraction pattern in which reflections, other than $hk0$, are diffuse along the direction perpendicular to the slabs. The diffuse streaks we observed in the Weissenberg photographs of szaibelyite (Fig. 1) then indicate that the crystal contains this sort of disorder. The cell dimensions and space groups of the above two simple polymorphic structures are compared in Table 6 together with those of szaibelyite.

According to P. B. Moore (private communication), the crystals of sussexite, $MnHBO_3$, from Sterling Hill, New Jersey, are isotypic with szaibelyite. Thus this structure is apparently the structure type for the crystals of the szaibelyite-sussexite series. Ellsworth and Poitevin (1921), however, observed parallel extinction of camsellite from British Columbia, and they suggested that the crystal would be orthorhombic. The powder diffraction lines of camsellite from the same locality can in fact be indexed (Takéuchi, 1957) by an orthorhombic cell of the second type in Table 6. Therefore, crystals of camsellite from this locality may well be orthorhombic. In conclusion, a reinvestigation of natural crystals of the szaibelyite-sussexite series is suggested bearing the above structural relationships in mind, so that the long standing mineralogical confusion of the series can be unravelled.

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References

BERGER, S. V. (1950) The crystal structure of cobaltpyroborate. *Acta Chem. Scand.* **4,** 1054–1065.

BRAITSCH, O. (1960) Die Borate und Phosphate im Zechsteinsalz Sudhannovers. *Fortschr. Mineral.* **38,** 190–191.

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

CRUICKSHANK, D. W. J. (1965) Errors in least-squares method. In, J. S. Rollet, Ed., *Computing Methods in Crystallography.* Pergamon Press, New York.

DONNAY, GABRIELLE, AND R. ALLMANN (1970) How to recognize O^{2-}, OH^-, and H_2O in crystal structures determined by X-rays. *Am. Mineral.* **55,** 1003–1015.

ELLSWORTH, H. V., AND E. POITEVIN (1921) Camsellite, a new borate mineral from British Columbia, Canada. *Trans. Royal Soc. Can. Sec. IV, Ser. III,* **15,** 1–18.

FEIT, W. (1891) Über Ascharit, ein neues Borsäure-Mineral. *Chem.-Ztg.* **15,** 327.

ITO, T. (1950) *X-ray Studies on Polymorphism.* Maruzen, Tokyo.

KUDOH, Y., AND Y. TAKÉUCHI (1973) Ascharite, $B_2H_2Mg_2O_6$. *Cryst. Struct. Comm.* **2,** 595–598.

PENG, CHIH-CHUNG, CHENG-YÜ WU, AND PI-HSING CHANG (1963) Crystal structure of ascharite. *Sci. Sinica,* **12,** 1761–1764 (In Russian).

PETERS, K. F. (1861) Geologische und mineralogische Studien aus dem südöstlichen Ungarn, insbesondere aus der Umgegend von Rézbánya. 2. *Teil. S. -B. Akad. Wiss. Wien,* **44,** 81–185.

SCHALLER, WALDEMAR T. (1942) The identity of ascharite, camsellite, and β-ascharite with szaibelyite, and some other relations of the magnesium borate minerals. *Am. Mineral.* **27,** 467–481.

TAKÉUCHI, Y. (1952) The crystal structure of magnesium pyroborate. *Acta. Crystallogr.* **5,** 574–581.

——— (1957) The interpretation of X-ray powder diffraction patterns of the szaibelyite-sussexite series. *Mineral. J.* **2,** 78–89.

——— (1958) Infrared absorption and structures of borate polyatomic ions. *Mineral. J.* **2,** 245–268.

WINCHELL, A. N. (1929) Camsellite and szaibelyite. *Am. Mineral.* **14,** 48–49.

WATANABE, TAKEO (1939) Kotoite, ein neues gesteinsbildendes Magnesiumborat. *Mineral. Petrogr. Mitt.* **50,** 448–463.

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