Crystal structure of a (001) twinned sussexite $Mn_2B_2O_4(OH)_2$ from the Kalahari Manganese Field South Africa

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Abstract

The crystal structure of a fibrous sussexite $Mn_{1.91}Mg_{0.09}B_2O_4(OH)_2$, space group $P2_1/c$, a = 3.287(1) Å, b = 10.718(2) Å, c = 12.866(3) Å, β = 94.75(3)° was solved and refined from single-crystal X-ray data collected on (001) twinned crystals. The refinement including hydrogen positions and anisotropic displacement parameters converged at an R-value of 4.95% for 2736 reflections. The density was calculated to 3.335 g · cm^{-3} with Z = 4. Sussexite is isotypic to szaibelyite $(Mg)_2B_2O_4(OH)_2$, both crystallizing in space group $P2_1/c$. Two non-equivalent chains of Mn/Mg octahedra (Mn1, Mn2) are connected by corners thus forming layers perpendicular to the c-axis. These sheets are linked by triangular pyroborate-groups $[B_2O_4(OH)]^{3-}$. In addition, hydrogen bridges stabilize the octahedral layer structure. The cleavage plane of sussexite is parallel to the octahedral layers. Average triangular B-O distances are 1.384 and 1.388 Å. Average octahedral Mn1-O and Mn2-O bond distances are 2.219 and 2.189 Å, respectively.

The twinning of sussexite can not be resolved under the polarizing microscope thus the twin components have either a very similar optic orientation or more probably, the twinning is on a submicroscopic scale.

Keywords: sussexite, structure determination, twinning, Kalahari Manganese Field.

Introduction

Originally, sussexite $(Mn_2B_2O_4(OH)_2)$ associated with pyrochroite, rhodochrosite, willemite and leucophoenicite was found in hydrothermal veinlets cutting massive franklinite ore at Franklin, Sussex County, New Jersey (PALACHE et al., 1960). It also occurs with seamanite as veinlets in hematite and cherty gangue at the Chicagon Mine, Iron County, Michigan (PALACHE et al., 1960). Balls of radiating sussexite have also been identified by X-ray powder diffraction from samples collected in pockets of the Hotazel Mine in the Kalahari Manganese Field, South Africa (VON BEZING et al., 1991). In Switzerland, sussexite was reported from Gonzen close to Sargans (canton St. Gallen) where it was found in veinlets together with wiserite, pyrochroite, and rhodochrosite within a rhodochrosite-hausmannite ore (EPPRECHT et al., 1959). According to cell dimensions and refractive indices (EPPRECHT et al., 1959) the Gonzen sussexite is almost a Mn end-member, whereas considerable Mg → Mn substitution was found

in samples from other localities (PALACHE et al., 1960). The Mg end-member $(Mg_2B_2O_4(OH)_2)$ is called szaibelyite (PETERS, 1861) originating as nodular masses in limestone at Rézbánya, Hungary. Both minerals form a solid solution series.

Former investigations of the szaibelyite $((\underline{Mg},Mn)_2B_2O_4(OH)_2)$ – sussexite $((\underline{Mn},Mg)_2 B_2O_4(OH)_2)$ group lead to a considerable confusion concerning different mineral species and true symmetry. These problems were probably caused by the fibrous appearance and intimate twinning or intergrowth of these minerals. The first quantitative information on this mineral group was obtained from chemical analyses and optical studies where refractive indices and the optical axial angle (2V) were determined. These measurements seem to confirm the distinction of various species: ascharite, β-ascharite, camsellite, szaibelyite, sussexite (WINCHELL, 1929; EPPRECHT et al., 1959). Subsequent reinvestigations using improved phase separation techniques accompanied with chemical, optical and X-ray powder

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Tab. 1 Various space groups and settings for szaibelyite reported in the literature.

Space group	a[Å]	b[Å]	c[Å]	β[°]	Transformed to
1.) orthorh.	10.34(1)	12.45(1)	3.21(1)		(b a–c)
2.) orthorh., B22₁2	3.14	10.42	25.05		(c/2cos(β – 90°)) -b a)
3.) monoclinic, P2₁/a	12.50	10.42	3.14	95.4	(a b c)
4.) monoclinic, P2₁/a	12.577(2)	10.393(2)	3.139(1)	95.88(2)	(a b c)

1.) TAKÉUCHI (1957)
2.) BRAITSCH (1960)
3.) PENG et al. (1963)
4.) TAKÉUCHI and KUDOH (1975)

studies showed that ascharite, β-ascharite, and camsellite were identical to szaibelyite $Mg_2B_2O_4$ $(OH)_2$ (SCHALLER, 1942).

The first information about the szaibelyite structure was published by TAKÉUCHI (1957) based on an X-ray powder pattern indexed in an orthorhombic setting with a = 10.34 Å, b = 12.45 Å, c = 3.21 Å. BRAITSCH (1960) suggested an orthorhombic B-centered cell with a = 3.14 Å, b = 10.42 Å, c = 25.05 Å, space group B22₁2 for ascharite (actually szaibelyite). In contrast, PENG et al. (1963) and TAKÉUCHI and KUDOH (1975) established a monoclinic cell, space group P2₁/a (P2₁/c in standard setting), a ~ 12.53 Å, b ~ 10.40 Å, c ~ 3.14 Å, β ~ 95° (Tab. 1). The former reported orthorhombic cells are either caused by small deviations from an orthogonal cell or artefacts due to twinning. Transformations relative to the monoclinic P2₁/a setting, first proposed by PENG et al. (1963), are given in table 1.

In a private communication of P.B. Moore (cited by TAKÉUCHI and KUDOH [1975]) it was assumed that sussexite is isotypic with szaibelyite. However, as suggested by TAKÉUCHI and KUDOH (1975), this problem has to be reinvestigated thus the long standing mineralogical confusion of the series can be unraveled. After the structure of szaibelyite has been determined by TAKÉUCHI and KUDOH (1975), the solution of the structure of sussexite is goal of the present study as a major step to disentangle the former discrepancies.

Experimental

The material investigated originates from the Nchwaning II Mine in the Kalahari Manganese Field, South Africa, and was donated to us by K.L. von Bezing. The sample is a dense half sphere (15 mm diameter) composed of radiating light pink needles of sussexite. In the center, sussexite is intergrown with calcite which encloses tiny bundles of a white fibrous mineral, probably inyoite, a hydrated calcium-borate. On the surface of the half sphere light brown platy fibers of sussexite form a pin-cushion-like crust. These fibres are approximately 100–230 × 5 – 40 × 5–40 μm in size. A selected crystal (193 × 37 × 35 μm) was mounted on a glass fibre with its elongated a-direction parallel to the fiber axis. Optical inspection (parallel and perpendicular to the fiber axis) under a polarizing microscope with crossed polarizers yielded parallel extinction and did not disclose any indication of twinning.

A Siemens P4R 4-circle-diffractometer with MoKα-radiation produced by a rotating anode (50 kV, 200 mA) was used for data collection in order to provide a high intensity X-ray beam for the small crystal. In a first test measurement an orthogonal supercell with a tripled c-axis was found (a = 3.287(1), b = 10.718(2), c = 38.50(1) Å). It was assumed that this supercell was a result of twinning. This assumption was mainly based on the observation of many systematic absences of orthorhombic indexed single-crystal reflections which were, however, not specific for any orthorhombic space group. In addition, symmetry equivalent reflections for orthorhombic setting showed significant discrepancies which could not be explained by absorption, extinction or multiple diffraction. Due to these different intensity contributions of the twinned individuals it was possible to determine twin law, cell dimensions, and space group for both individuals. The measured crystal exhibited twinning parallel (001) leading to an overlap of 0kl and 3kl reflections for both individuals. In the final data collection, we measured each twin-component in its own setting by collecting two different data sets comprising 4035 reflections. TAKÉUCHI and KUDOH (1975) refined the structure of szaibelyite also from a twin but considered only one twin fragment by assuming a 1:1 volume ratio for the twin individuals, thus using halved intensities for the superimposed hk0 reflections (P2₁/a setting). In the present study on sussexite we refined the X-ray intensity contributions of both individuals (Tab. 2).

Tab. 2 Cell parameters and refinement parameters.

	Cell parameters from single crystal measurements	Refined cell parameters from Guinier powder data
a	3.287(1) [Å]	3.288(1) [Å]
b	10.718(2) [Å]	10.704(3) [Å]
c	12.866(3) [Å]	12.883(8) [Å]
ß	94.75(3) [°]	94.62(4) [°]
Z	4	
density	3.335 [g/cm³]	
volume	451.71 [Å³]	
cell wt	887.43	
twinning contribution	0.544 : 0.466	
crystal size	193 × 37 × 35 [μm]	
diffractometer with rotating anode current, voltage	50 [kV], 200 [mA]	
reflections[Fo > 4σ(Fo)]	2736	
F(000)	427	
[1]wR2	0.1033	
[2]R1	0.0495	
[3]Goof	1.037	

[1]wR2 $= \{[\sum w\,(Fo^2 - Fc^2)^2] / [\sum w\,(Fo^2)^2]\}^{1/2}$
[2]R1 $= (\sum ||Fo| - |Fc||) / (\sum |Fo|)$
[3]Goof $= \{[\sum w\,(Fo^2 - Fc^2)^2] / [n - p]\}^{1/2}$

Structure determination

Direct methods were successfully applied using the program SHELXTL PC™ (SIEMENS, 1990) to localize the Mn sites in sussexite. For this purpose only the dataset from one twin component without the superimposed reflections of the type 0kl and 3kl was used. Starting values for O and B positions were obtained by subsequent refinements accompanied with difference Fourier analyses. For the final refinement of the twinned crystal based on F^2_{obs} we used the program SHELXL93 (SHELDRICK, 1993) in its HKLF 5 option. This refinement is described in more detail because the strategy is not well documented in the program description. After measuring the two data sets each in its own setting, we declared one individual to the master crystal (#1) and the other one to #2. Diffraction intensities of the second crystal (#2) are needed to correct its influences on the intensities of the superimposed reflections (0kl and 3kl). Both crystal diffraction data were merged onto one dataset where each reflection was characterized by h, k, l, F^2_o, $\sigma^2_{(Fo)}$, and an additional flag (1 or 2) which determines wether the corresponding reflection originates from the first individual (flag = 1) or from the second (flag = 2). Reflections which are influenced by both individuals were grouped into pairs where h_2, k_2, l_2, $(F^2_{o1}, \sigma^2_{(Fo)1})$ from crystal #2 are given first with

flag = -2 followed by the indices and F^2_{o1}, $\sigma^2_{(Fo)1}$ of crystal #1 with flag = 1 etc. With this coding the influence of the twin components on the bulk reflection intensity (0kl, 3kl) is calculated. F^2_{o1}, $\sigma^2_{(Fo)1}$ may have the same values for two superimposed reflections since only the values in the last line (flag = 1) are taken into consideration. In addition, the input file of SHELXL93 needs a BASF-instruction to refine the twin-components where the calculated value is 1-(contribution of crystal #1).

According to the above strategy, the structure of (001) twinned sussexite was refined using neutral atom scattering factors to an conventional R-value of 4.95% (Tab. 2). The measured diffraction data for this twin can not be considered excellent because of the small crystal dimensions and the corresponding low reflection intensities accompanied with relatively high standard deviations. Nevertheless, the two hydrogen atoms could be determined from difference Fourier synthesis. According to an electron microprobe analysis for Mn, Mg, and Si, an average formula $Mn_{1.91}Mg_{0.09}B_2O_4(OH)_2$ was obtained. In addition, the electron microprobe analyses revealed enigmatic but significant 1 wt% SiO_2, corresponding to 0.04 Si p.f.u. It is assumed that the analyzed Si content results from submicroscopic inclusions or is enriched on twin boundaries. Because of the significant Mg content, the Mn/Mg ratio was al-

Tab. 3	Atomic positions for sussexite.

Atom	x	y	z	sof
M1	.2296(2)	.13888(6)	.50637(4)	0.921(8) Mn + 0.079(9) Mg
M2	.7154(2)	.41978(6)	.41041(4)	0.891(8) Mn + 0.109(8) Mg
B1	.7548(13)	.1672(4)	.1410(3)	1.00
B2	.6263(14)	.0476(5)	.3073(3)	1.00
O1	.7729(9)	.0645(3)	.0780(2)	1.00
O2	.7608(9)	.2873(3)	.1044(2)	1.00
O3	.7186(9)	.1522(3)	.2485(2)	1.00
O4	.6026(9)	.4523(3)	.2429(2)	1.00
O5	.7236(9)	.0438(3)	.4129(2)	1.00
O6	.2099(9)	.2932(3)	.4035(2)	1.00
H4**	.330(17)	.6156(31)	.8025(31)	1.00
H4*	.322(18)	.6175(46)	.8053(40)	1.00
H6**	.815(17)	.7537(39)	.1644(16)	1.00
H6*	.795(18)	.7608(39)	.1497(39)	1.00

*	non restraint positions of the hydrogen atoms
**	restraint positions of the hydrogen atoms

Tab. 4	Anisotropic displacement parameters for sussexite.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}
M1	.0084(3)	.0081(4)	.0095(3)	.0002(3)	.0013(2)	-.0005(2)	.0087(2)
M2	.0092(3)	.0119(4)	.0085(3)	-.0006(3)	.0015(2)	.0003(3)	.0098(2)
B1	.0083(20)	.0067(32)	.0064(15)	.0025(17)	.0015(15)	-.0016(14)	.0071(10)
B2	.0116(24)	.0228(35)	.0117(18)	.0012(18)	.0050(16)	.0011(17)	.0151(12)
O1	.0152(14)	.0115(18)	.0123(12)	-.0020(14)	.0015(12)	-.0001(10)	.0130(7)
O2	.0154(14)	.0122(18)	.0146(12)	.0019(14)	.0035(11)	.0014(11)	.0140(7)
O3	.0274(17)	.0140(19)	.0112(11)	-.0033(14)	.0032(11)	-.0005(11)	.0174(7)
O4	.0258(18)	.0154(20)	.0100(12)	.0039(12)	-.0006(12)	-.0037(10)	.0172(8)
O5	.0152(13)	.0142(19)	.0124(11)	.0021(12)	.0019(11)	.0013(11)	.0139(7)
O6	.0149(13)	.0127(18)	.0114(11)	-.0026(14)	.0008(11)	.0024(11)	.0130(6)

lowed to vary for Mn1 and Mn2 sites. These population refinements lead to 8% Mg on Mn1 and 11% Mg on Mn2. The last cycles of the refinement were calculated in duplicate. In the first model the H positions remained unconstrained with a fixed isotropic displacement parameter. This refinement yielded 1.02 Å for the O4-H4 distance and 0.77 Å for the O6-H6 distance. In order to obtain reliable H...O bridging distances, a second type of refinement was performed using restrained hydrogen positions (CECCARELLI et al., 1981), fixed at a distance of 0.970(5) Å from the oxygen atoms of the hydroxyl-groups (O4 and O6, respectively). In this type of refinement U_{iso} of H was also fixed at 0.05 Å².

Results

It was proposed that the more or less Mn-rich members of the sussexite-szaibelyite-group are part of an isomorphic solid solution series

(SCHALLER, 1942). Hitherto there was the problem that the Mg-rich members seemed to have a monoclinic structure whereas an orthorhombic space group was assumed for the Mn-rich ones. This reinvestigation clearly shows that szaibelyite and sussexite form a solid solution series with the same space group (P2₁/c). Single-crystal X-ray data yielded following cell dimensions for sussexite: a = 3.287(1), b = 10.718(2), c = 12.866(3) Å, β = 94.75(3)°. Refined atomic coordinates and atomic displacement parameters are given in tables 3 and 4. Selected interatomic distances and angles for sussexite are compared with corresponding values for szaibelyite in table 5. For better comparison with szaibelyite we adopted the atom numbering scheme of TAKÉUCHI and KUDOH (1975).

Because a monoclinic indexed powder pattern of sussexite is not existent as yet, the monoclinic lattice parameters were also refined from 27 powder reflections recorded with an asymmetric transmission-type Guinier camera (FeKα₁-radia-

Tab. 5 Selected interatomic distances and angles in sussexite and szaibelyite.

Atom1	Atom2	Distances of sussexite [Å]	Distances of szaibelyite (TAKÉUCHI and KUDOH, 1975) [Å]	At1-At2-At3	Angles of sussexite [°]	Angles of szaibelyite (TAKÉUCHI and KUDOH, 1975) [°]
M1	O6	2.116(3)	2.037(5)			
	O2	2.214(3)	2.115(6)			
	O2a	2.217(3)	2.118(6)			
	O5	2.216(3)	2.132(6)			
	O5a	2.218(3)	2.140(5)			
	O5b	2.333(3)	2.214(5)			
average		2.219	2.126			
M2	O4	2.184(3)	2.085(5)			
	O6	2.125(3)	2.035(6)			
	O6a	2.141(3)	2.048(6)			
	O1	2.156(2)	2.051(5)			
	O1a	2.246(3)	2.139(5)			
	O1b	2.284(3)	2.161(5)			
average		2.189	2.087			
O2	H4**	1.633(38)				
	H4*	1.586(51)				
O4	O2	2.594(4)	2.564(7)			
	H4**	0.970(37)				
	H4*	1.016(51)				
O3	H6**	2.122(43)				
	H6*	2.298(52)				
O6	O3	2.887(4)	2.812(7)			
	H6**	0.968(26)				
	H6*	0.769(50)				
B1	O1	1.371(5)	1.351(9)	O1-B1-O2	123.3(3)	125.1(7)
	O2	1.371(5)	1.357(10)	O1-B1-O3	120.0(4)	119.5(6)
	O3	1.408(4)	1.413(9)	O2-B1-O3	116.7(3)	115.4(8)
average		1.384	1.374			
B2	O5	1.370(5)	1.337(9)	O3-B2-O4	118.0(3)	116.7(5)
	O4	1.395(5)	1.403(10)	O3-B2-O5	121.1(4)	121.7(5)
	O3	1.399(5)	1.396(10)	O4-B2-O5	120.7(4)	121.3(5)
average		1.388	1.379			
				B1-O3-B2	131.5(3)	130.6(7)

*   non restrained hydrogen atoms
** restrained hydrogen atoms

tion). Indices of powder reflections were calculated from the refined atomic coordinates using the program LAZY PULVERIX (YVON et al., 1977). Powder X-ray intensities were estimated by eye. The cell dimension refinement from powder data was carried out with the program GITTER (HUMMEL, 1988) (Tabs 2 and 6).

Description of the structure

The structures of szaibelyite (TAKÉUCHI and KUDOH, 1975) and sussexite (this paper) consist of

two different types of slightly distorted (Mg,Mn) octahedra which form distinct chains (chain A and B) parallel to the a-axis. Each octahedron is connected with four edges (M1: 2 × O5-O5, and 2 × O5-O2; M2: 2 × O1-O1, and 2 × O6-O1) to four additional octahedra of the same kind thus leading to double chains. In addition, M1 octahedra (A chain) share one corner (O6) with M2 octahedra (B chain) and M2 octahedra share two corners (O6) with M1 octahedra, respectively, leading to undulated octahedral layers. Type A and B chains are corner linked (O6) parallel to b (Fig. 1). In sussexite the Mn1-O distances of the

Tab. 6 X-ray powder pattern for sussexite recorded with a FeKα₁ Guinier-camera.

d_{obs}	d_{calc}	I_{obs}	I_{calc}	hkl
6.43	6.42	10	10	0 0 2
5.36	5.35	3	2	0 2 0
3.97	3.97	4	2	0 1 3
3.44	3.44	4	1	0 3 1
3.34	3.34	6	3	0 2 3
3.12	3.12	4	2	0 3 2
3.05	3.02	4	1	1 0-2
2.906	2.906	3	1	1 1-2
2.773	2.771	7	5	1 2-1
2.741	2.741	5	2	0 3 3
	2.734		2	1 1 2
2.694	2.693	5	4	1 2 1
2.682	2.676	1	1	0 4 0
2.632	2.630	6	3	1 2-2
2.494	2.501	6	2	1 2 2
	2.497		4	0 1 5
2.471	2.470	1	1	0 4 2
2.415	2.418	5	1	1 2-3
	2.414		3	1 3 0
2.268	2.270	1	1	1 2 3
	2.269		1	0 4 3
2.139*	2.140	1	1	0 0 6
2.064–2.053*	2.063	1	1	1 4-1
	2.056		1	0 4 4
1.986–1.980*	1.987	1	1	0 2 6
	1.987		0.5	1 3-4
1.793	1.792	3	2	1 5 0
1.748	1.746	1	2	1 5-2
1.707	1.707	1	1	1 5 2
	1.707		1	1 1 6
1.651	1.651	1	2	1 3-6
1.618	1.619	1	1	2 0-2
1.517	1.518	1	1	0 7 1
1.510	1.510	1	1	2 2-3
	1.509		0.3	1 6 2

* one very broad line on the film

A chain are between 2.116 Å and 2.333 Å, the Mn2-O distances of the B chain range between 2.125 Å and 2.284 Å. The shortest Mn-O distance is always formed by the chain-connecting oxygen O6. The resulting octahedral sheets are linked by triangular pyroborate groups $[B_2O_4(OH)]^{3-}$ and stabilized by hydrogen bonds. The two BO_3 triangles intervening the layers (Fig. 2) have a B-O-B angle of 131.5(3)°. The B-O distances within the triangles are between 1.370 Å and 1.408 Å with O-B-O angles between 116.7° and 123.3°. Oxygen O4, connecting a Mn2 octahedron with the B2 triangle, belongs to an OH-group forming a hydrogen bridge to O2 with an O4-O2 distance of 2.594(4) Å. If H4 is restrained at a distance of 0.97 Å to O4 a bridging distance H4...O2 of 1.633(38) Å is calculated. The second OH group is O6-H6 forming a weak hydrogen bridge to

O3 with H6...O3 of 2.12 Å (distance O3-O6 = 2.887 Å).

The assignment of OH-groups was also tested by the bond valence method of BROWN and ALTERMATT (1985). Corresponding bond valences and valence sums are given for physically meaningful restrained H positions in table 7.

Discussion

The observed orthorhombic supercell (a = 3.287, b = 10.718, c = 38.50 Å) is caused by the fact that (001) twinning leads not only to a superposition of the 0kl but also of the 3kl reflections of both monoclinic individuals. This 3kl superposition can only occur if 3 $a^* \cdot \sin(\beta - 90) = c^*$ which is roughly the case for sussexite where 3 $a^* \cdot \sin(\beta - 90) = 0.0758$ and $c^* = 0.0780$. Using the cell dimensions for szaibelyite by TAKÉUCHI and KUDOH (1975), 3 $a^* \cdot \sin(\beta - 90) = 0.0984$ and $c^* = 0.0799$, thus these values are significantly different and 3kl overlap is not expected. In addition, TAKÉUCHI and KUDOH (1975) used CuKα radiation for their data collection leading to a higher spatial resolution within the reciprocal lattice.
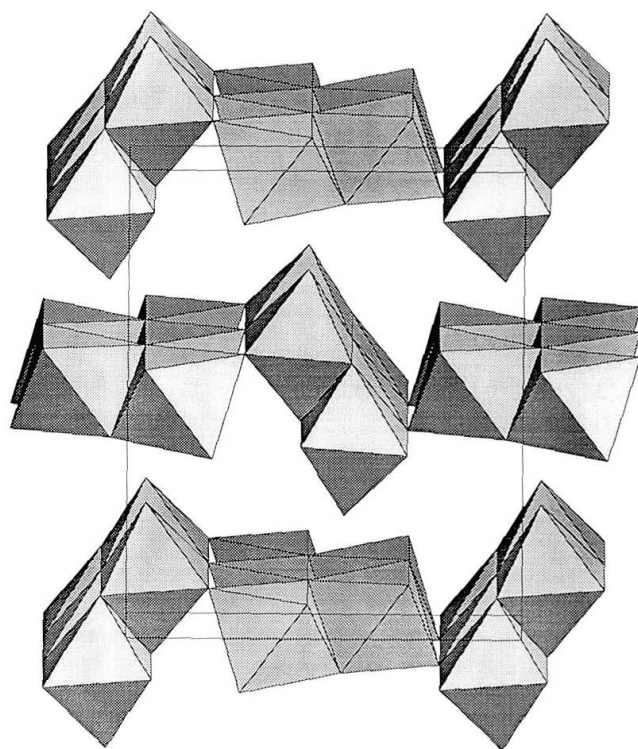

Fig. 1 M1 and M2 octahedra form two distinct double chains (A and B chain) parallel to the a-axis. These chains are cornerlinked with each other building undulated sheets perpendicular to the c-axis. The view is along the a-axis with b across and c down (Computer program Atoms by DOWTY [1992]).
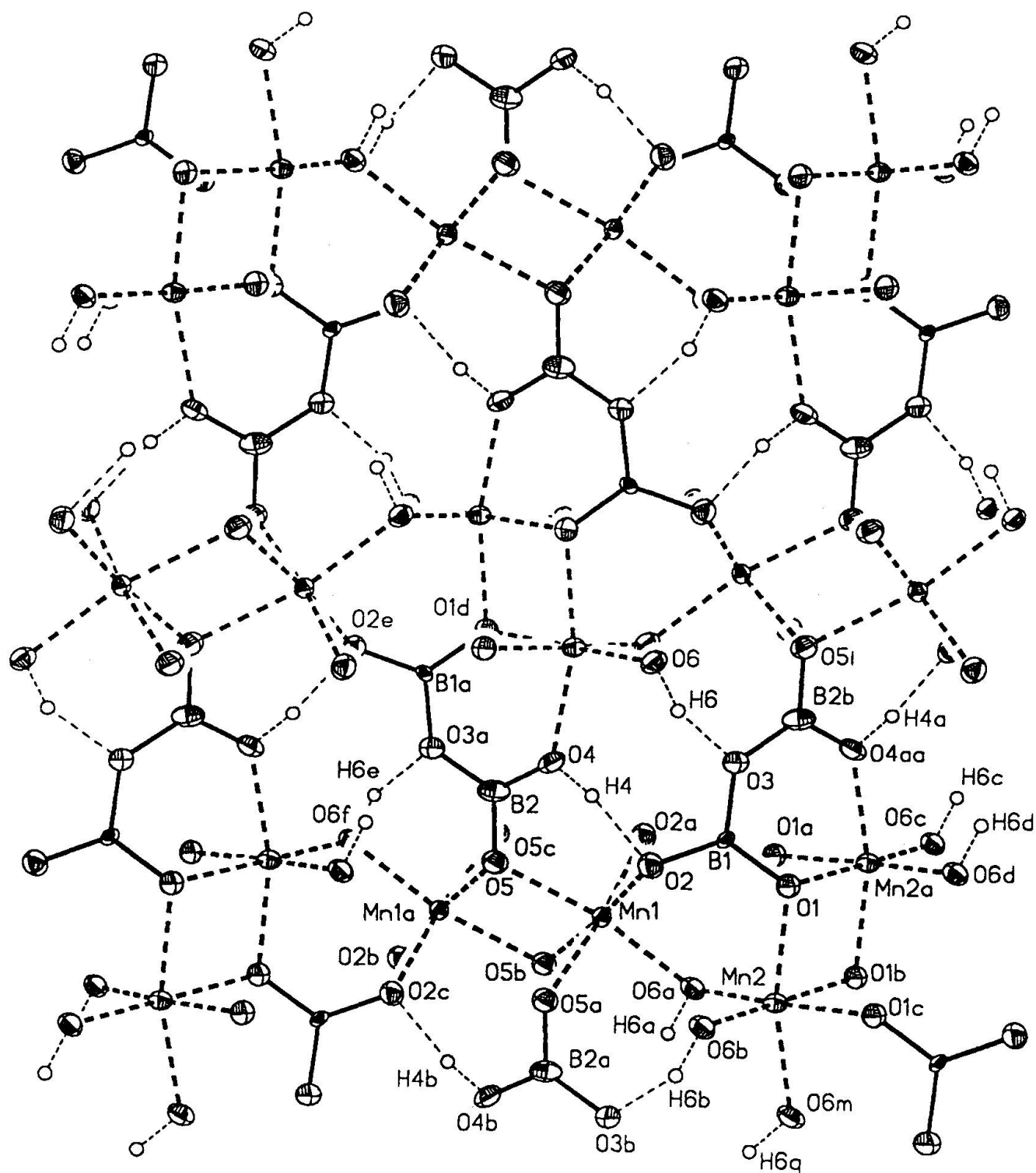
Fig. 2 The structure of sussexite is displayed with anisotropic displacement parameters for B, O and Mn, and isotropic displacement parameters for H.

The M1/M2 octahedra are represented by dashed solid bonds, B-O bonds are shown with solid lines, O-H...O bridges with dashes. The view is along the a-axis with b across and c down.

Figure 3 shows the twinning superposition of the reciprocal lattices of the two monoclinic sussexite individuals. The a- and b-axes are superimposed, only the direction of the c-axis varies. The twinning of two individuals in that way produces an apparent orthorhombic supercell. Inspection of several sussexite crystals by single-crystal X-ray methods indicated that the macroscopic crystal is always composed of two twin components in a ratio close 1:1. It is surprising that this twinning

Tab. 7 Bond valences for sussexite.

	Mn1	Mn2	B1	B2	Σ*	H4**	H6**	Σ**
O1		0.372	1.001		1.928			
O1a		0.292						
O1b		0.263						
O2	0.318		1.001		1.634	0.131		1.765
O2a	0.315							
O3			0.905	0.927	1.832		0.035	1.867
O4		0.345		0.937	1.282	0.788		2.070
O5	0.316			1.003	1.864			
O5a	0.315							
O5b	0.230							
O6	0.414	0.404			1.205		0.793	1.998
O6a		0.387						
Σ	1.908	2.063	2.907	2.867				

* without considering hydrogen atoms
** with restrained hydrogen atoms

cannot be resolved under the polarizing microscope. This could indicate that the optical orientation is almost parallel for both twin components or more probably, the twinning is on a submicroscopic scale. The sharp single-crystal X-ray reflections seem to exclude a random submicroscopic type of twinning in the range of few unit cells.

Twinning of isotypic szaibelyite was already discussed by TAKÉUCHI and KUDOH (1975). These authors argue that the szaibelyite structure can be divided in two unit slabs related to each other by an inversion center between the sheets. Because of pseudosymmetry, these slabs may be repeated by a twofold screw operation (parallel to the a-axis [3.139 Å]) instead of the inversion center. If this type of polysynthetic twinning takes place on the scale of two unit slabs (one unit cell of szaibelyite), an orthogonal cell (a = 3.139, b = 10.393, c = 25.022 Å) results which, however, has only monoclinic symmetry with the unique axis running parallel to a (3.139 Å). On the basis of the orthorhombic 38 Å supercell for sussexite, one could argue that twinning may take place on the scale of three unit slabs. However, as mentioned above, the sussexite supercell is an artefact caused only by the incidental similarity between $3\,a^* \cdot \sin(\beta - 90)$ and c^*. In case of sussexite, we do
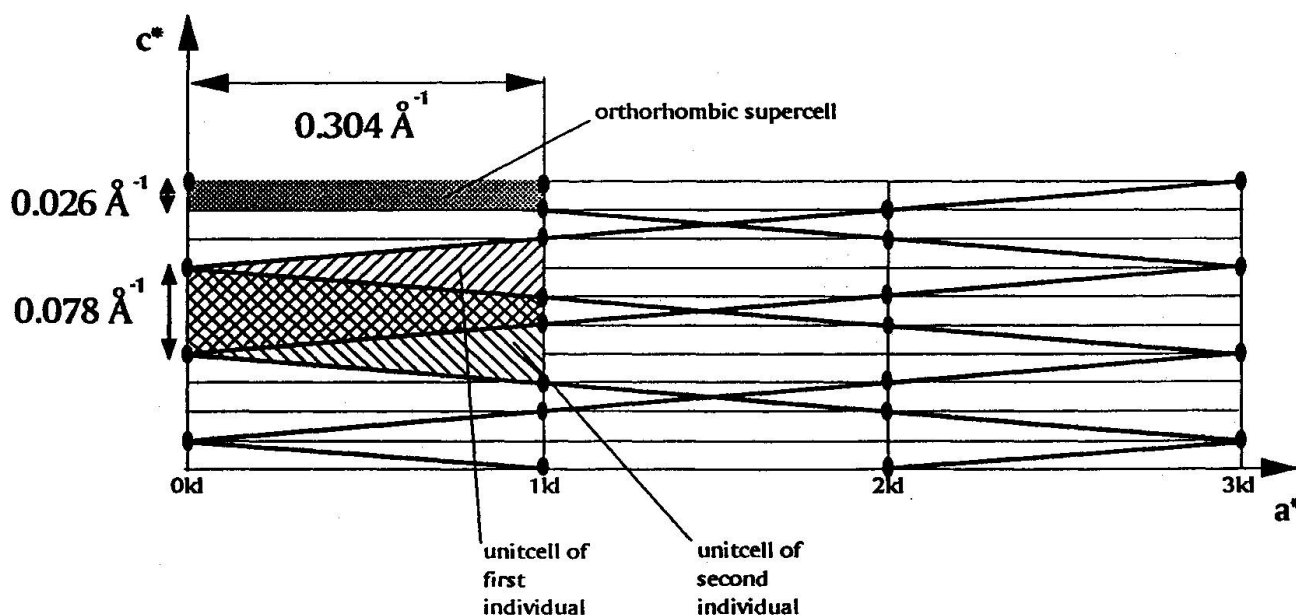

Fig. 3 Schematic drawing of the sussexite twinning in reciprocal space with the reciprocal axes of the orthorhombic supercell. The reciprocal lattices and unit cells of the two twin individuals are displayed in the same picture to indicate their respective orientation. The intensities of hkl reflections, with h = 3n, are influenced by both individuals. All other X-ray reflections are only caused by one individual.

Tab. 8   Distortion of the Mn/Mg octahedra and BO_3 triangles

	Sussexite				Szaibelyite			
	Mn1	Mn2	B1	B2	Mg1	Mg2	B1	B2
ABL[Å]	2.219	2.189	1.384	1.388	2.126	2.087	1.374	1.379
BLD[%]	1.7	2.3	1.2	0.9	1.7	2.1	1.9	2.0
AEL[Å]	3.132	3.087	2.395	2.403	3.000	2.944	2.377	2.386
ELD[%]	3.1	4.4	0.8	0.2	3.0	4.1	1.0	0.1
BLD/ELD	0.5	0.5	1.5	4.5	0.6	0.5	1.9	20.0
CAD[%]			1.8	1.0			2.8	1.4
TAD[%]			1.9	0.3			1.7	0.1
CAD/TAD			0.9	3.3			1.6	14.0

ABL   average of bond length
AEL   average edge length
BLD   bond length distortion
ELD   edge length distortion
TAD   triangle angular distortion (O-O-O angles)
CAD   central atom angular distortion (O-B-O angles)

$$BLD = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{|BL_i - ABL|}{ABL} \%$$

n = number of bonds of central atom
BL_i = individual bond length

$$CAD = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{|angle_i - 120°|}{120°} \%$$

n = number of angles adjacent to central atom

$$ELD = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{|EL_i - AEL|}{AEL} \%$$

n = number of bonds of central atom
EL_i = individual edge length

$$TAD = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{|angle_i - 60°|}{60°} \%$$

n = number of corners of polyhedron

not find any indication for a polymorphic super-structure because these twin domains have different scattering contributions, thus a polysynthetic twin must be assumed. In addition, TAKÉUCHI and KUDOH (1975) assume that if twinning takes place in a random fashion, reflections other than 0kl should be diffuse as observed for szaibelyite. In a recent TEM and X-ray powder study of szaibelyite from Rézbánya, Hungary, (DÓDONY and LOVAS, 1994) the twin domains were reported in the range of a hundred Å. Based on these arguments, the Kalahari sussexite without diffuse reflections could be interpreted as a polysynthetic twin with twin domains below the optic resolution but large enough to produce a sharp diffraction pattern. These twinning arguments may also explain why sussexite-szaibelyite minerals show mostly parallel extinction under the polarizing microscope in spite of their monoclinic symmetry. The parallel extinction of sussexite minerals was erroneously used as indicator for orthorhombic symmetry.

Polyhedral distortion in sussexite and szaibelyite

In the following, the structural differences between the end members of the solid solution series, szaibelyite and sussexite, caused by the Mg → Mn substitution are discussed. In general, the octahedral bondlengths for sussexite are about 0.1 Å longer (Tab. 5) than the corresponding ones for szaibelyite. An individual octahedral distortion parameter was calculated from the M-O bondlengths (bond length distortion BLD) according to WENGER and ARMBRUSTER (1991) and RENNER and LEHMANN (1986).

The same calculation was done for octhedral edges (edge length distortion ELD) by regarding the ligand to ligand distances within the polyhedron. With this kind of calculation we obtained a distortion description which is detached from the size of the octahedron. It is obvious from tables 5 and 8 that BLD values for Mn (sussexite) and Mg (szaibelyite) show the same low distortion of

1.7% for M1 and about 2% for M2. A similar pattern is found for ELD values yielding 3.1% (Mn1), 3.0% (Mg1), 4.4% (Mn2), and 4.1% (Mg2), respectively. This means that the octahedra in sussexite and szaibelyite show only minor deviations from an ideal octahedron with $m\bar{3}m$ symmetry. The low ratio of BLD/ELD (ca. 0.5) indicates that the cation resides in the center of the octahedron. Obviously the Mn2, Mg2 octahedra of the B-chain are slightly more distorted than Mn1 and Mg1 but in general the Mn, Mg layers are building a relaxed and stable part of the structure.

The distortions of the BO_3 triangles are within a range of 0%–2% for BLD and ELD (Tab. 7). Considering the ratio of BLD/ELD the calculated values are at least two times higher than those for the octahedra. Most surprisingly, there is the large BLD/ELD value of 20 for B2 in szaibelyite. Performing the same distortion calculation for angles (Tab. 8), we obtain a high CAD/TAD ratio of 14 for B2 in szaibelyite. This means that the central atom is shifted out of the center of the triangle, which itself has only a minor distortion (ELD = 0.1%). The reason for the distortion in szaibelyite is the short distance of 1.337 Å between B2 and O5. Sussexite also shows a slight trend towards this anomaly of the B2-triangle (Tab. 8). Average B1-O and B2-O distances in sussexite are 0.01 Å longer than in szaibelyite.

ZOBETZ (1982, 1990) examined 44 compounds to find out wether the triangular borate group shows a characteristic aplanarity value like in carbonate- (ZEMANN, 1981) or nitrate-groups (JAROSCH and ZEMANN, 1983). ZOBETZ (1982, 1990) noticed, that boron moves out of the triangular oxygen plane towards an additional oxygen, provided this oxygen occurs in a distance blow 3.0 Å above the boron. This oxygen apparently attracts the boron and causes in boracites (with an additional B-O distance of ca. 2.0 Å) an out of plane displacement of the boron up to 0.4 Å (ZOBETZ, 1982, 1990). However in sussexite, examined in this paper, there is no oxygen in such an exposed position that could influence the boron. Nevertheless BO_3 triangles show an unexpected large aplanarity value (0.01 to 0.04 Å). The [O1-O2-O3]-B1 pyramid (0.002, 0.010 Å in szaibelyite, sussexite) is more planar than the [O3-O4-O5]-B2 pyramid (0.043 Å) in both, sussexite and szaibelyite. The two oxygen planes are slanted by an angle of 32.9(4)° in sussexite and 32.0(7)° in szaibelyite.

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