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The crystal structure of zinc orthoborate, $Zn_3(BO_3)_2$

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Auszug

$Zn_3(BO_3)_2$ hat die Gitterkonstanten $a = 23{,}40_6$, $b = 5{,}04_8$, $c = 8{,}38_1$ Å und $\beta = 97°32'$. Die Elementarzelle der Raumgruppe Ic enthält 8 Formeleinheiten. Die Struktur wurde mit Hilfe von BUERGERS Minimumfunktion und von Fouriersynthesen in (010)- und (001)-Projektionen bestimmt und durch dreidimensionale Differential-Fouriersynthesen verfeinert. Für 802 beobachtete Interferenzen ergab sich $R = 0{,}132$ als Endwert.

Die Sauerstoffionen in den Ecken von $(BO_3)^{3-}$-Dreiecken gehören auch $(ZnO_4)^{6-}$-Tetraedern an. Es gibt regelmäßige Tetraeder, die gemeinsame Ecken haben, und deformierte mit gemeinsamen Kanten. Diese Tetraeder bilden Bänder.

Abstract

Zinc orthoborate crystallizes in the monoclinic system, space group Ic, with eight molecules in a cell of dimensions $a = 23.40_6$, $b = 5.04_8$, $c = 8.38_1$ Å and $\beta = 97°32'$. The structure has been determined by BUERGER's minimum function and Fourier synthesis in projections (010) and (001), and refined by three-dimensional differential Fourier synthesis, yielding a final R value of 0.132 for 802 observed reflections.

The structure of $Zn_3(BO_3)_2$ consists of $(BO_3)^{3-}$ triangles which share a common vertex with $(ZnO_4)^{6-}$ tetrahedra. There are two kinds of tetrahedra: regular ones, sharing common vertices, and distorted ones sharing common edges. These tetrahedra form ribbons of interconnected units.

Introduction

The binary system $ZnO—B_2O_3$ has been studied by several authors. INGERSON, MOREY and TUTTLE (1948) reported two compounds: $ZnO \cdot B_2O_3$ and $5ZnO \cdot 2B_2O_3$. TOROPOV and KONOVALOV (1949) reported three compounds: $3ZnO \cdot B_2O_3$, $ZnO \cdot B_2O_3$ and $ZnO \cdot 3B_2O_3$. HARRISON and HUMMEL (1956) found that two compounds exist, $5ZnO \cdot 2B_2O_3$ and $ZnO \cdot B_2O_3$, both of them exhibiting low- and high-temperature polymorphic forms. BAUER (1963) reported the

compounds $ZnO \cdot 2B_2O_3$, $ZnO \cdot B_2O_3$ and $3ZnO \cdot B_2O_3$. WEIR and SCHROEDER (1964) found the compounds $ZnO \cdot 2B_2O_3$, $4ZnO \cdot 3B_2O_3$ and $5ZnO \cdot 2B_2O_3$. Finally FAYOS, GARCIA-BLANCO and RIVOIR (1966) investigated the system using calcined samples and a quench technique, obtaining single crystals. In this case three compounds were reported: $Zn_4O(BO_2)_6$, whose crystal structure was determined by SMITH, GARCIA-BLANCO and RIVOIR (1964); a phase of low temperature with approximate composition $ZnO \cdot 2B_2O_3$, and the zinc orthoborate, $Zn_3(BO_3)_2$.

The purpose of the present paper is to report the crystal structure of this new phase, $Zn_3(BO_3)_2$.

Experimental

Single crystals of $Zn_3(BO_3)_2$ were extracted from quenched $5ZnO \cdot 2B_2O_3$ mixtures. They were colourless plates elongated along the b axis and frequently twinned. Single-crystal oscillation and Weissenberg photographs showed monoclinic symmetry. The observed reflections, hkl with $h+k+l=2n$, $h0l$ with $h=2n$ (and $l=2n$), and $0k0$ with $k=2n$, are characteristic of the space groups $I2/c$ and Ic. A rather close agreement between the F_o and F_c was obtained, as may be seen later, with space group Ic, which is considered as final. The lattice constants obtained from a powder diffractogram are: $a=23.406 \pm 0.010$ Å, $b=5.048 \pm 0.005$ Å, $c=8.381 \pm 0.005$ Å, $\beta = 97°32' \pm 3'$. The experimental density, determined by the pycnometric method, is $4.15\ g \cdot cm^{-3}$ and the number of molecules per unit cell is eight, corresponding to an x-ray density of $4.24_6\ g \cdot cm^{-3}$.

The intensity data were collected from an untwinned crystal with cross section 0.011×0.004 cm, using Cu$K\alpha$ radiation, $\mu_{Cu} = 182\ cm^{-1}$. Equi-inclination Weissenberg data were obtained by the multiple-film technique for reflections $h0l$, $h1l$, $h2l$, $h3l$, $h4l$ and $hk0$, which were measured photometrically. The intensity data were independently corrected for Lorentz and polarization effects. Absorption corrections, assuming cylindrical crystal shape, were unsuccessfull. Relative $|F_{hkl}|$ values were placed in absolute scale with the calculated $|F_{hkl}|$, in the three-dimensional refinement of the structure.

Determination and refinement of the structure

A Patterson projection $P(xz)$ was made with 126 $|F_{h0l}|^2$'s. Assuming that the space group was the centrosymmetric $I2/c$, minimum functions (BUERGER, 1959) were obtained from the three inversion

peaks. The x,z coordinates for the zinc atoms were determined from the M_8^{ABC}, Fig. 1.

A first Fourier synthesis $\varrho(xz)$ was made with the signs obtained from the zinc coordinates and this map not only shows the peaks for the heavier atoms but also various peaks for the lighter ones.

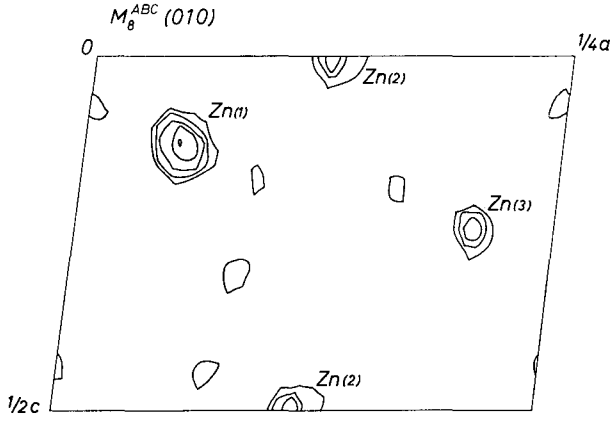

Fig. 1. Minimum function projection, $M_8^{ABC}(xz)$

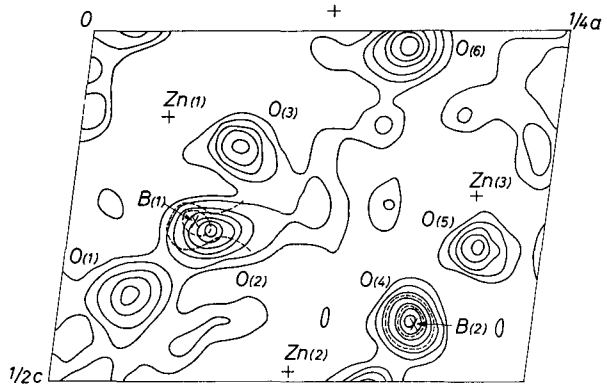

Fig. 2. Difference-density projection on (010) computed with F_o—$F_{c\,(heavy)}$, space group $I\,2/c$

Several Fourier and difference Fourier syntheses were made; Fig. 2 shows the final one. The six oxygen atoms in the asymmetric unit are represented. The boron atoms B_1 and B_2 coincide with the oxygen atoms O(2) and O(4). A difference Fourier without the

contribution of the oxygen atoms showed these boron atoms, Fig. 2. The discrepancy factor with zinc, oxygen and boron atoms was $R_{h0l} = 0.183$.

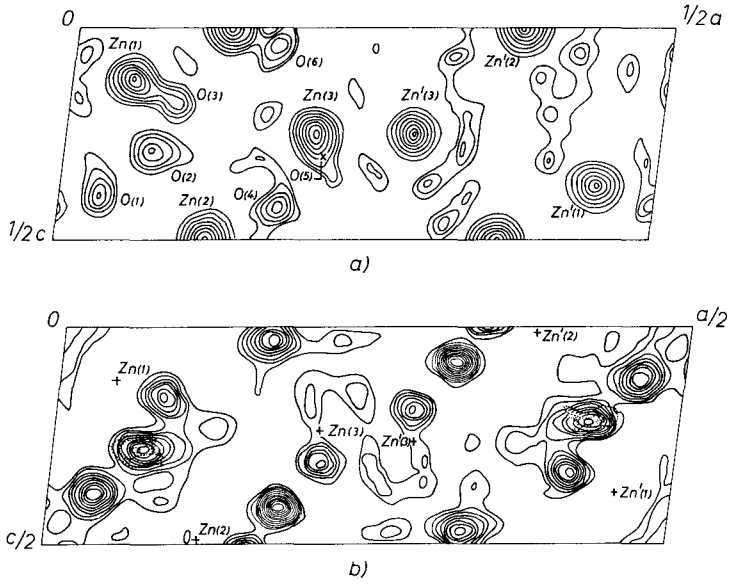

Fig. 3. (*a*) Two-dimensional Fourier projection, and (*b*) difference Fourier projection on (010) in space group *Ic*

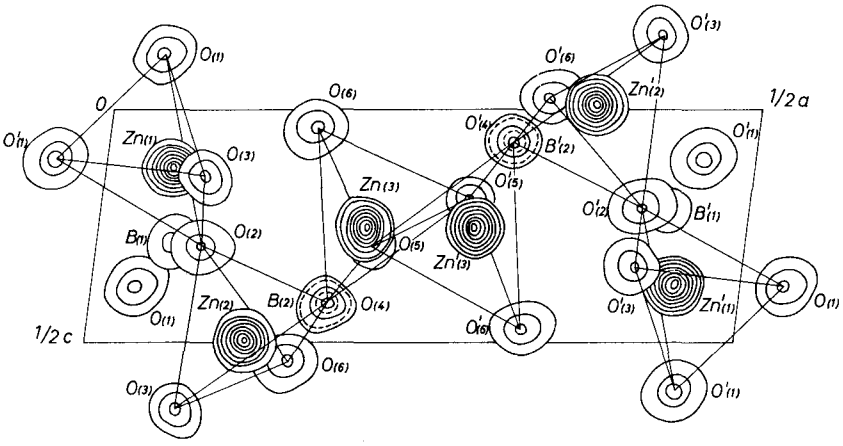

Fig. 4. Composite diagrams of the three-dimensional electron-density function. Contours are drawn at intervals of 6 eÅ^{-3} starting with 1 eÅ^{-3} (for Zn at 14 eÅ^{-3} intervals), zero omitted

The y coordinate for the above mentioned atoms was also obtained from the Patterson projection $P(xy)$. For the refinement of these parameters, Fourier and difference Fourier syntheses was employed. The final R index in this case is 0.238.

With these coordinates a coordination structure with triangles (BO_3) and tetrahedra (ZnO_4) was obtained except for the zinc atom near to the origen. This is due to the two-fold axis in $x = 0$, $z = 1/4$ in space group $I2/c$, which prevents the tetrahedral coordination. Therefore new computations were tried by using the noncentrosymmetric group Ic. However it was thought that, at least for the six zinc atoms, some pseudosymmetry with respect to the group $I2/c$ would exist for otherwise the previous results could not have been obtained.

New Fourier syntheses in the noncentrosymmetric group decreased the R index to $R_{h0l} = 0.131$ and $R_{hk0} = 0.170$. Figures 3*a* and 3*b* represent the Fourier and difference Fourier projections on (010) in space group Ic. The structure obtained in this space group permits tetrahedral coordination for all zinc atoms.

The refinement was carried out using 802 reflections recorded by rotation about the b axis. Table 1 shows the schematic form of this refinement. The R index decreased to the end value of 0.132 (omitting fifteen reflections affected by extinction). Table 2 gives the $|F_{obs}|$ and the $|F_{cal}|$ values. Table 3 shows the final atomic parameters with the individual isotropic thermal parameters. Finally, Fig. 4 represents the last three-dimensional Fourier synthesis.

Table 1

Number of cycles	Synthesis used	Temperature factor	R
1—4	three-dimensional Fourier synthesis	$B = 0$	0.180
5	three-dimensional differential Fourier synthesis	$B = 0$	0.163
6	three-dimensional Fourier synthesis	Individual and isotropic	0.156
7—12	three-dimensional differential Fourier synthesis	Individual and isotropic	0.132

Table 2. *Observed and calculated structure amplitudes*

h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$
- 4 0 0	68.6	57.8	0 0 8	310.8	331.3	-23 1 4	104.4	93.0	3 1 10	44.4	48.6
- 6	88.2	67.2	2	53.7	46.4	-21	51.3	30.3	2 2 0	28.7	40.5
- 8	248.6	245.6	4	20.6	50.3	-13	109.6	84.5	6	31.2	26.7
-10	45.4	36.1	6	82.8	71.4	-13	80.1	59.5	8	59.9	52.0
-12	361.8	440.5	8	19.4	44.0	-11	133.2	125.8	10	41.3	27.4
-14	153.8	139.9	12	273.8	284.8	- 9	93.9	74.7	12	222.2	313.2
-16	75.7	66.4	14	22.7	42.6	- 7	67.9	52.7	14	89.3	108.6
-18	49.8	55.8	16	33.2	39.1	- 5	44.8	24.8	18	71.2	51.1
-22	72.9	56.7	-14 0 10	120.9	151.3	- 3	65.5	49.1	24	138.1	187.1
-24	298.4	284.8	-12	47.0	69.4	- 1	230.6	267.1	26	94.9	98.5
-26	142.6	126.5	-10	91.4	94.9	1	144.3	123.4	-25 2 1	32.6	28.7
-28	63.2	64.6	- 8	163.2	178.9	3	109.0	80.7	-23	223.9	246.9
-28 0 2	149.9	128.2	- 6	117.2	120.1	7	117.5	104.4	-21	67.1	48.3
-26	249.1	206.6	- 4	118.7	100.8	9	47.1	37.7	-17	37.6	35.7
-24	78.0	63.0	- 2	128.3	134.2	11	115.3	89.8	-15	109.2	97.8
-22	233.3	205.4	0	34.9	44.4	13	110.3	86.1	-13	127.7	152.9
-20	144.3	122.7	2	13.8	14.5	15	73.5	60.3	-11	213.7	304.7
-18	120.1	122.7	4	117.6	146.3	23	95.4	84.6	- 9	118.8	124.1
-16	130.4	131.1	6	74.9	86.2	25	33.8	33.7	- 7	132.1	127.7
-14	264.4	301.4	3 1 0	156.5	169.4	-24 1 5	150.2	167.3	- 5	86.1	55.2
-12	144.1	140.5	5	55.5	41.3	-22	206.4	252.0	- 3	146.2	126.8
-10	237.1	252.4	7	31.9	32.9	-20	130.4	130.9	- 1	109.0	100.6
- 8	334.1	390.0	9	164.5	198.4	-18	69.7	61.4	1	237.6	263.6
- 6	279.5	263.6	11	29.3	23.0	-16	44.1	49.1	3	61.2	64.0
- 4	140.6	91.8	13	95.7	68.2	-14	128.1	102.8	5	148.2	160.5
- 2	206.7	192.1	15	105.9	83.1	-12	232.2	229.8	7	43.3	50.8
0	54.7	35.3	17	87.9	79.6	-10	195.3	180.1	9	112.7	113.3
2	80.2	61.1	21	177.4	145.3	- 8	251.1	255.9	11	117.4	119.5
4	368.1	579.2	27	67.9	58.6	- 6	104.7	86.9	13	150.4	129.8
6	150.4	99.3	29	50.5	59.1	- 4	113.9	100.2	15	246.1	257.0
8	196.1	185.5	-26 1 1	134.0	134.6	- 2	91.3	64.6	17	149.0	127.3
10	186.4	184.3	-20	248.9	291.4	0	191.7	226.7	19	57.8	40.2
12	157.4	153.9	-18	43.1	44.3	2	183.6	199.5	21	64.6	41.9
14	108.0	97.5	-16	155.3	140.6	4	225.6	310.7	23	15.7	21.1
16	326.2	352.8	-14	180.4	235.8	6	32.5	40.1	25	51.4	41.1
18	61.4	56.7	-12	20.7	20.2	8	139.9	103.7	27	103.6	142.8
20	210.2	173.1	-10	83.5	58.5	10	86.8	60.5	-28 2 2	65.5	80.0
22	79.3	80.4	- 8	179.2	338.3	12	166.8	155.0	-26	123.2	121.5
24	131.6	106.1	- 6	155.6	238.3	16	262.2	279.3	-24	63.7	50.2
26	95.6	64.1	- 4	166.4	178.3	18	100.9	84.1	-22	134.0	131.2
28	190.0	203.7	- 2	190.5	222.4	20	76.7	74.6	-20	107.8	115.7
-28 0 4	15.4	15.7	0	16.6	11.9	-25 1 6	41.4	36.7	-18	77.2	61.5
-26	157.2	118.9	2	39.4	26.9	-23	68.3	59.2	-16	105.9	92.7
-24	185.7	174.6	4	216.8	339.6	-21	59.4	54.2	-14	149.5	154.3
-22	228.0	203.5	6	169.0	203.3	-19	112.0	99.4	-10	158.6	195.4
-20	132.3	116.1	8	183.4	211.0	-17	51.5	18.6	- 8	174.4	208.7
-18	123.9	117.5	10	172.3	199.9	-15	70.0	56.6	- 6	111.6	90.2
-16	27.7	19.6	12	87.6	83.8	-13	99.0	89.3	- 4	144.0	129.0
-14	272.4	305.2	14	57.2	50.8	-11	52.7	41.1	- 2	210.3	200.5
-12	235.4	216.7	16	178.5	152.0	- 9	33.8	26.6	0	18.4	24.4
-10	275.3	276.3	18	292.0	289.8	- 7	182.3	155.5	2	72.2	67.6
- 8	249.2	220.1	20	130.7	97.9	- 1	64.9	42.2	4	258.3	305.6
- 6	69.7	52.1	24	141.0	138.3	3	98.1	72.7	6	18.8	9.7
- 4	210.3	163.7	26	98.4	91.6	5	97.1	83.5	8	139.6	148.4
- 2	335.7	325.6	28	57.0	77.9	9	78.0	52.5	10	73.5	77.1
0	175.2	150.6	-29 1 2	47.5	49.8	15	85.8	68.0	12	94.5	83.9
2	309.0	344.0	-27	83.0	73.4	17	130.7	116.0	14	71.3	54.8
4	192.7	174.4	-25	32.5	43.8	19	65.7	63.4	16	198.5	182.6
6	61.1	50.9	-19	70.4	52.3	-24 1 7	116.8	141.0	18	27.6	22.4
8	240.4	259.8	-17	157.8	137.1	-22	49.0	53.0	20	116.7	96.4
10	201.8	233.1	-13	67.2	61.0	-20	65.0	68.2	22	63.5	61.6
12	59.5	89.9	- 9	37.3	29.1	-18	181.5	208.8	24	56.2	49.5
14	193.1	197.1	- 7	181.6	181.7	-16	133.7	131.6	-25 2 3	114.2	130.0
18	46.8	39.9	- 5	211.4	258.5	-12	128.5	109.5	-23	49.5	38.4
20	254.8	221.9	- 3	141.8	123.6	-10	144.9	134.8	-21	69.7	66.3
22	169.4	141.0	- 1	28.0	18.8	- 8	42.9	46.0	-19	159.8	191.1
24	135.2	156.7	3	141.5	115.4	- 6	216.8	213.6	-17	72.8	64.4
26	119.7	144.9	5	37.1	22.0	- 4	194.2	176.7	-15	107.9	101.3
-26 0 6	35.8	49.0	7	176.4	184.7	0	94.7	78.7	-13	136.3	141.2
-24	64.2	65.9	11	108.3	95.0	2	167.8	157.0	-11	61.0	57.6
-22	56.4	48.9	13	116.1	101.4	4	113.2	97.3	- 9	125.4	117.7
-20	166.3	148.0	19	102.5	77.6	6	177.8	179.2	- 7	176.8	189.7
-16	205.8	208.3	23	42.9	30.1	8	226.9	240.6	- 5	44.9	45.2
-14	98.8	87.9	25	94.2	82.1	14	175.2	171.5	- 3	165.8	152.7
-12	124.2	119.0	-28 1 3	129.8	170.2	16	54.4	42.8	- 1	137.1	117.0
-10	127.1	124.0	-26	100.7	98.4	18	52.2	58.3	1	164.0	142.1
- 8	244.2	241.8	-24	63.9	50.1	-21 1 8	48.4	56.6	3	155.8	146.4
- 6	177.7	165.0	-18	54.2	39.3	-19	37.1	46.4	5	185.2	192.6
- 4	367.6	408.4	-16	247.6	341.3	-15	96.6	89.3	7	29.5	21.3
- 2	25.7	26.3	-14	41.5	31.1	- 9	113.5	105.7	9	207.5	240.3
0	25.9	41.5	-12	191.9	252.9	- 3	108.7	88.2	11	111.9	80.2
2	212.4	238.9	-10	31.4	30.0	3	126.2	110.9	13	158.2	128.1
4	43.4	73.1	- 8	115.3	114.6	7	59.4	48.3	15	154.8	127.1
6	114.7	115.7	- 6	93.0	66.2	9	91.6	88.9	17	93.4	70.4
8	212.4	217.9	- 4	210.9	250.2	11	48.1	32.0	19	104.0	89.8
10	166.6	144.7	- 2	100.4	82.9	15	32.2	31.1	21	141.9	147.4
12	81.4	77.5	0	239.2	272.8	-18 1 9	68.3	70.4	23	26.7	43.0
14	163.7	148.9	2	89.1	59.9	-16	67.9	71.3	25	95.1	103.9
16	74.6	90.5	4	138.5	124.6	-14	111.6	134.2	-26 2 4	104.9	115.9
18	63.0	60.8	6	93.4	81.8	- 8	180.3	201.3	-24	109.2	111.9
20	127.5	132.5	8	234.0	282.7	- 6	122.7	125.1	-22	97.3	96.6
22	105.4	103.6	10	188.0	203.2	- 4	68.1	67.6	-20	62.9	58.9
-20 0 8	11.8	23.3	12	341.7	355.9	- 2	158.4	173.6	-18	41.6	34.9
-18	68.9	71.7	14	45.5	36.4	4	180.8	182.4	-14	148.5	142.6
-16	79.7	74.2	16	81.6	52.1	6	165.5	192.3	-12	144.6	145.7
-14	110.8	95.8	18	137.7	118.3	8	107.2	107.0	-10	172.6	165.3
-12	293.4	305.6	20	76.9	82.5	10	107.0	117.2	- 8	129.5	125.7
-10	154.2	131.5	22	196.1	192.7	- 5 1 10	107.2	117.5	- 6	89.3	75.1
- 6	38.0	11.0	24	138.8	140.0	- 3	39.9	40.4	- 4	140.9	129.8
- 2	137.0	96.6	26	43.7	50.0	1	46.0	49.3	- 2	201.3	220.6

Table 2. *(Continued)*

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 4	122.9	122.6	13 3 0	46.1	25.4	-14 3 5	46.9	32.6	21 4 1	79.4	73.1
2	193.5	218.4	15	192.4	179.1	-12	76.3	57.7	-18 4 2	46.6	33.1
4	45.3	41.9	17	108.2	95.6	-10	88.3	66.9	-16	45.6	45.9
6	53.8	37.6	19	44.3	40.6	- 8	90.8	86.4	-14	48.2	30.9
8	135.5	113.6	21	250.0	257.3	- 4	28.8	20.3	-12	68.0	64.5
10	153.3	136.8	23	62.5	59.2	- 2	37.8	30.5	-10	39.9	41.9
12	120.6	111.8	-26 3 1	48.5	47.9	0	78.1	54.8	- 8	53.7	51.8
14	143.1	140.1	-24	27.1	19.6	2	34.3	31.4	- 6	79.4	74.4
16	51.2	38.4	-20	115.2	105.6	4	92.3	79.5	- 4	68.0	73.2
20	137.4	115.4	-18	70.8	67.2	6	105.3	96.3	- 2	16.4	5.6
22	101.7	96.2	-16	20.8	20.5	8	33.3	24.5	0	23.6	33.7
24	61.4	83.4	-14	109.0	87.2	10	40.0	30.6	2	62.7	64.4
-25 2 5	82.3	98.7	-12	29.8	21.2	12	83.2	72.5	4	72.0	63.0
-23	60.2	54.2	-10	80.9	78.8	14	64.3	50.6	6	18.4	39.6
-21	113.5	137.9	- 8	120.1	129.0	16	101.3	95.4	8	45.8	47.1
-19	132.1	139.2	- 6	73.8	65.1	18	57.8	69.6	10	28.6	18.0
-17	122.5	116.5	- 4	22.7	19.5	20	28.9	30.7	14	36.2	45.9
-15	108.6	92.6	- 2	36.2	23.3	-21 3 6	63.8	62.6	16	64.9	48.0
-13	142.7	136.9	0	30.6	10.4	-19	165.9	192.8	18	60.4	48.0
-11	36.1	21.6	2	21.1	31.7	-17	65.8	54.7	-23 4 3	30.3	24.3
- 9	169.7	150.6	4	130.0	148.3	-15	82.9	82.0	-19	169.5	192.2
- 7	59.0	41.1	6	22.0	38.2	-13	117.2	123.8	-17	119.0	110.4
- 5	208.1	182.8	8	78.8	54.1	-11	154.5	120.4	-15	152.6	153.7
- 3	123.9	117.8	10	64.3	70.1	- 7	254.1	292.2	-13	169.3	165.8
- 1	169.0	143.4	12	78.1	50.5	- 5	76.4	48.6	-11	104.8	80.9
1	137.6	112.7	16	60.2	60.9	- 3	82.1	70.6	- 9	179.1	148.3
3	174.0	143.5	18	87.3	72.0	- 1	106.9	86.1	- 7	145.6	131.6
5	41.2	21.2	20	52.7	44.8	3	140.3	122.9	- 5	186.9	191.6
7	204.2	211.2	24	56.2	48.3	5	187.8	221.7	- 1	122.0	121.7
9	128.5	112.1	-25 3 2	53.7	50.1	7	107.2	99.0	1	56.3	50.1
11	115.1	92.3	-23	24.2	18.2	9	49.6	49.3	3	101.1	95.4
13	131.1	127.0	-19	166.7	170.2	13	27.4	28.3	5	216.3	203.9
15	86.7	70.6	-17	213.1	234.6	15	97.5	96.9	7	46.9	32.5
17	105.4	89.2	-15	89.6	89.8	17	147.0	196.4	9	191.7	176.5
19	167.3	169.7	-13	117.3	96.7	-18 3 7	81.5	87.1	11	122.4	106.6
-24 2 6	52.5	52.3	- 9	63.3	48.6	-16	78.1	92.7	13	192.9	179.6
-22	48.5	45.3	- 7	194.6	205.6	-12	44.2	40.8	15	121.6	100.6
-20	114.1	121.3	- 5	281.4	420.2	-10	62.5	57.0	17	103.6	107.0
-16	143.7	150.0	- 3	176.9	160.5	- 8	67.9	58.6	19	114.1	114.5
-14	45.3	30.3	- 1	22.8	16.6	- 6	54.7	39.1	-22 4 4	38.5	30.9
-12	93.6	80.0	1	143.6	119.4	- 4	86.2	87.5	-20	37.7	42.5
-10	101.1	82.3	3	124.7	114.5	0	98.6	75.5	-18	36.7	49.4
- 8	133.7	119.0	5	83.7	66.1	2	43.5	33.7	-14	34.8	13.4
- 6	78.4	62.8	7	234.4	346.4	4	28.5	10.9	-12	31.5	33.7
- 4	209.8	216.7	9	37.9	27.0	6	62.1	57.1	-10	25.2	27.3
- 2	49.3	40.9	11	121.6	98.1	8	66.0	68.3	- 8	55.2	56.0
2	128.8	109.4	13	178.7	153.0	12	23.6	24.2	- 4	26.2	17.8
4	99.1	95.3	15	111.8	84.7	14	32.2	32.2	0	51.3	56.8
6	82.8	69.0	17	81.8	72.7	-17 3 8	66.5	88.7	2	35.3	14.0
8	134.9	126.3	19	204.8	203.4	-15	118.9	137.7	4	64.4	45.2
10	81.9	73.1	21	71.2	53.9	-13	26.6	21.4	8	54.7	55.5
12	36.9	21.6	23	112.0	100.9	-11	31.9	17.2	10	29.5	29.1
14	119.7	113.3	-26 3 3	31.7	22.7	- 9	167.3	215.8	12	65.0	51.6
16	37.8	73.9	-24	48.3	52.3	- 7	63.4	66.8	18	26.2	29.4
18	36.8	41.4	-20	31.0	11.4	- 5	22.9	26.1	-19 4 5	91.3	98.3
20	61.4	82.4	-18	57.1	58.5	- 3	177.4	204.5	-17	112.5	124.8
-21 2 7	36.1	38.1	-16	71.7	59.5	- 1	28.8	22.5	-15	98.0	99.2
-17	96.3	101.5	-14	35.8	39.8	1	29.7	20.5	-13	128.9	137.2
-15	151.2	191.3	-10	40.7	29.5	3	155.8	180.1	-11	131.8	133.4
-13	148.9	144.6	- 6	88.4	82.9	5	30.8	28.2	- 9	178.9	184.9
-11	44.5	47.0	- 4	151.5	142.8	7	45.1	56.5	- 7	87.4	70.1
- 9	82.3	75.7	- 2	60.3	55.0	9	141.4	180.3	- 5	181.8	172.4
- 5	29.2	42.1	0	113.2	91.3	11	140.9	40.0	- 3	42.2	39.7
- 3	176.0	161.0	2	27.8	29.9	- 8 3 9	85.9	92.5	- 1	209.4	185.8
- 1	162.0	159.8	4	76.8	62.3	- 6	44.5	48.1	1	111.7	106.6
1	86.8	73.3	6	103.5	98.7	- 4	23.6	25.6	3	167.6	159.5
3	112.3	94.5	8	58.3	67.3	- 2	77.4	64.8	5	66.5	53.6
7	77.0	71.5	10	52.9	52.4	0	14.0	13.7	7	228.4	259.3
9	49.5	55.5	12	120.1	90.3	2	34.4	26.3	9	120.6	105.9
11	214.2	243.1	14	76.3	57.6	4	68.8	87.8	11	68.4	60.3
13	66.3	61.5	18	19.7	26.6	4 4 0	18.8	18.4	13	138.7	144.3
15	50.1	51.3	20	52.3	55.5	6	19.2	14.3	15	61.4	75.9
17	58.3	63.8	22	40.2	39.0	8	58.9	46.7	17	53.9	73.2
-16 2 8	47.6	36.2	-25 3 4	56.0	58.2	10	55.9	52.0	-18 4 6	24.9	29.0
-14	70.3	61.3	-23	144.2	167.1	12	17.1	28.4	-14	46.2	56.9
-12	159.5	200.5	-21	57.9	48.1	14	31.7	31.2	- 6	67.8	62.7
-10	25.3	31.1	-19	107.8	100.8	16	44.6	42.0	- 4	72.4	53.1
0	192.4	222.2	-17	29.1	22.6	18	20.9	25.0	- 2	41.0	48.4
6	46.7	26.3	-15	165.1	169.3	22	53.5	48.2	2	41.8	31.2
8	37.0	35.0	-13	153.5	149.9	-23 4 1	172.7	230.6	4	63.2	61.8
12	126.3	160.4	-11	231.5	264.6	-21	52.2	33.1	6	44.6	39.4
-15 2 9	62.4	65.8	- 9	38.0	21.3	-19	52.6	52.2	8	32.8	31.1
-13	39.3	37.4	- 7	108.1	90.8	-17	93.4	76.8	12	36.5	45.5
-11	131.0	175.2	- 5	67.1	49.7	-15	38.0	37.5	14	13.1	18.6
- 9	53.4	52.2	- 3	116.9	104.4	-13	172.9	142.7	-15 4 7	124.9	194.5
- 7	48.8	45.8	- 1	232.6	360.5	-11	249.6	305.2	-13	94.9	121.6
- 5	77.8	83.5	1	201.2	252.0	- 9	119.1	97.7	-11	25.8	34.3
- 1	47.2	49.1	3	116.4	111.7	- 7	81.8	77.2	- 9	71.1	76.5
1	162.1	192.5	5	43.9	29.5	- 5	21.9	16.6	- 5	80.2	88.3
3	98.5	104.9	7	168.6	141.2	- 3	107.1	110.6	- 3	139.7	158.2
5	88.7	97.6	9	49.2	49.1	- 1	68.8	73.1	- 1	181.3	213.8
9	56.8	77.0	11	210.8	223.3	1	171.4	276.8	1	54.5	40.7
- 8 2 10	72.0	113.0	13	151.5	137.4	3	153.6	200.7	3	116.1	115.7
- 6	47.6	60.2	15	134.4	122.7	5	121.2	114.7	5	60.5	56.7
- 4	41.0	57.2	17	41.3	17.5	7	33.0	49.9	7	28.6	41.7
- 2	63.3	84.8	19	88.3	85.1	9	123.3	103.8	9	81.8	105.3
3 3 0	220.6	351.3	21	22.9	34.7	11	45.4	33.7	-10 4 8	51.0	61.5
5	80.9	61.6	-22 3 5	80.6	77.4	13	210.0	194.2	- 2	51.4	51.4
7	88.3	75.7	-20	75.0	79.5	15	219.2	214.3	0	22.1	20.1
9	282.3	332.5	-18	50.9	46.2	17	141.7	129.4			
11	56.9	49.0	-16	23.5	20.3	19	89.4	72.1			

Table 3. *Fractional atomic coordinates and thermal parameter*

Atom	x	y	z	B
Zn(1)	0.0503 0.0002*	0.8354 0.0012*	0.1255 0.0005*	0.17
Zn(2)	0.1261 0.0002*	0.6819 0.0012*	0.4945 0.0005*	0.00
Zn(3)	0.2087 0.0002*	0.6942 0.0016*	0.2502 0.0006*	0.04
Zn(1′)	0.4514 0.0002*	0.3236 0.0012*	0.3762 0.0005*	0.12
Zn(2′)	0.3712 0.0002*	0.1890 0.0012*	−0.0036 0.0005*	0.00
Zn(3′)	0.2898 0.0002*	0.1929 0.0012*	0.2519 0.0005*	0.08
O(1)	0.0351 0.0008*	0.2208 0.0071*	0.3791 0.0027*	0.45
O(2)	0.0816 0.0017*	0.5984 0.0051*	0.2923 0.0021*	1.15
O(3)	0.0767 0.0011*	0.1833 0.0091*	0.1422 0.0032*	0.02
O(4)	0.1843 0.0009*	0.9186 0.0053*	0.4169 0.0031*	0.00
O(5)	0.2124 0.0009*	0.3263 0.0130*	0.2987 0.0032*	0.00
O(6)	0.1617 0.0010*	0.6469 0.0085*	0.0393 0.0030*	0.60
O(1′)	0.4620 0.009*	0.6983 0.0087*	0.1035 0.0021*	0.23
O(2′)	0.4178 0.0014*	0.0765 0.0048*	0.2145 0.0020*	0.00
O(3′)	0.4184 0.0010*	0.6879 0.0071*	0.3414 0.0026*	0.00

Table 3. *(Continued)*

Atom	x	y	z	B
O(4′)	0.3143	0.4090	0.0881	0.10
	0.0009*	0.0048*	0.0023*	
O(5′)	0.2840	0.7977	0.1871	0.10
	0.0008*	0.0127*	0.0032*	
O(6′)	0.3361	0.2011	0.4721	0.00
	0.0008*	0.0049*	0.0026*	
B(1)	0.0643	0.3321	0.2863	0.22
	0.0013*	0.0063*	0.0036*	
B(2)	0.1856	0.1743	0.4152	0.00
	0.0018*	0.0079*	0.0032*	
B(1′)	0.4323	0.7927	0.2181	0.14
	0.0014*	0.0079*	0.0039*	
B(2′)	0.3141	0.6907	0.0784	0.00
	0.0015*	0.0075*	0.0031*	

* Estimated standard deviations

Description and discussion of the structure

The following points concerning structure of zinc orthoborate are now well established:

(*a*) The BO_3^{3-} anions form triangles with the boron atom in the center of the triangle.

(*b*) Each Zn^{2+} cation is surrounded by four oxygen atoms forming a tetrahedron.

(*c*) In this configuration, each oxygen atom belongs to two tetrahedra and a triangle. These form in this way chains in which the tetrahedra share vertices or edges of the tetrahedra, and the triangles share edges. This configuration agrees with the results previously found in the other compounds in which the BO_3^{3-} anions form triangles while the zinc atoms are coordinated to oxygen atoms in tetrahedra, octahedra or both.

Figure 5 represents a view of the structure down to the *b* axis, and Fig. 6 shows the asymmetric unit of the structure seen along the

c axis. A pseudosymmetry in (010) projection exists with a false center in position $\frac{1}{4}\frac{1}{4}$. ERIKS and MACGILLAVRY (1954) found a structural pseudosymmetry in the crystal structure of $N_2O_5 \cdot 3SO_3$, whose space group is Cc, with strong pseudosymmetry which introduces a false center in one of the projections.

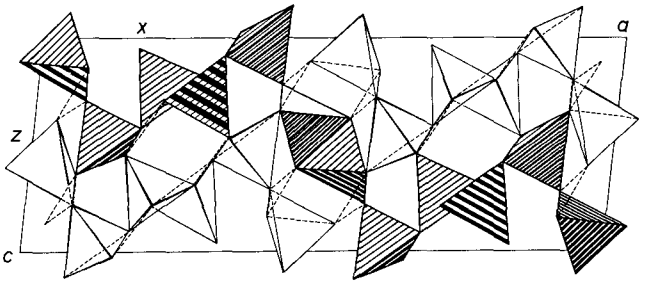

Fig. 5. A view of the structure down to the b axis

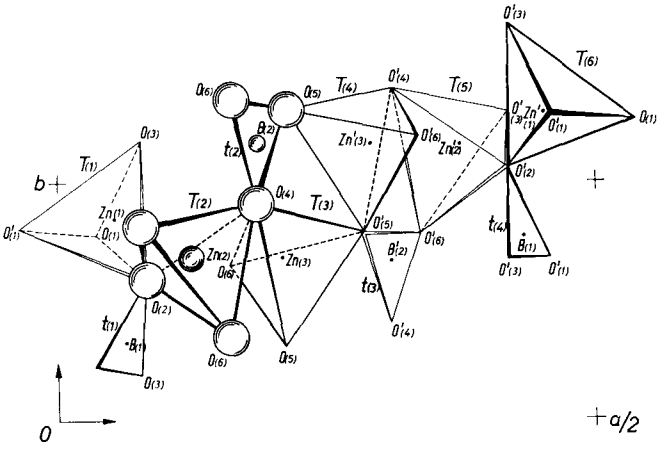

Fig. 6. The asymmetric unit of the structure along the c axis

The interatomic distances with their standard deviations, in each tetrahedron and in each triangle, are given together with the mean values in Table 4. In T_1 and T_6 the common distance of 2.71 Å for O(1)—O(1′) is somewhat short. Therefore we do not take this distance into account in the calculation of the mean value. Table 5 shows the O—Zn—O angles in the tetrahedra and the O—B—O and O—O—O angles in the triangles. These distances and angles agree with the results previously found in the other compounds (see Table 6).

Table 4. *Bond lengths in tetrahedra and triangles*

Symmetry code

I	x	y	z	A	x	$1-y$	$-\frac{1}{2}+z$
B	x	$1+y$	z	C	$-\frac{1}{2}+x$	$\frac{3}{2}-y$	z
D	x	$1-y$	$\frac{1}{2}+z$	E	x	$2-y$	$-\frac{1}{2}+z$
F	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z	G	x	$2-y$	$\frac{1}{2}+z$

Tetrahedron I			Tetrahedron II		
Zn(1)I—O(1)A	2.069	* 7 Å	Zn(2)I—O(2)I	1.916	* 7 Å
Zn(1)I O(1′)C	2.058	* 7	Zn(2)I O(3)D	1.926	* 7
Zn(1)I O(2)I	1.911	* 7	Zn(2)I O(4)I	1.985	* 7
Zn(1)I O(3)B	1.861	* 7	Zn(2)I O(6)D	1.873	* 7
O(1) O(1′)	2.706	*36	O(2) O(3)	3.149	*46
O(1) O(2)	3.608	*39	O(2) O(4)	2.970	*39
O(1) O(3)	3.067	*36	O(2) O(6)	2.884	*39
O(2) O(1′)	3.199	*39	O(3) O(4)	3.379	*41
O(2) O(3)	3.206	*43	O(3) O(6)	3.260	*46
O(3) O(1′)	3.286	*38	O(4) O(6)	3.102	*34
Zn(1) O	1.97	* 7	Zn(2) O	1.93	* 7
O O	3.28	*38	O O	3.12	*41
Tetrahedron III			**Tetrahedron IV**		
Zn(3)I—O(4)I	1.942	* 8	Zn(3′)B—O(5)B	2.019	* 7
Zn(3)I O(5)I	1.901	* 8	Zn(3′)B O(4′)B	1.900	* 7
Zn(3)I O(6)I	1.970	* 8	Zn(3′)B O(5′)I	2.067	* 7
Zn(3)I O(5′)I	1.976	* 8	Zn(3′)B O(6′)B	2.014	* 7
O(4) O(5)	3.244	*53	O(5) O(4′)	3.175	*53
O(4) O(6)	3.426	*34	O(5) O(5′)	3.349	*52
O(4) O(5′)	3.272	*34	O(5) O(6′)	3.129	*53
O(5) O(6)	2.842	*48	O(4′) O(5′)	3.297	*42
O(5) O(5′)	3.124	*52	O(4′) O(6′)	3.360	*30
O(6) O(5′)	3.062	*52	O(5′) O(6′)	3.252	*31
Zn(3) O	1.95	* 8	Zn(3′) O	1.99	* 7
O O	3.16	*45	O O	3.26	*43
Tetrahedron V			**Tetrahedron VI**		
Zn(2′)B—O(2′)B	2.081	* 7	Zn(1′)I—O(1)F	1.969	* 7
Zn(2′)B O(3′)E	1.916	* 7	Zn(1′)I O(1′)D	1.892	* 7
Zn(2′)B O(4′)B	1.966	* 7	Zn(1′)I O(2′)I	1.932	* 7
Zn(2′)B O(6′)A	2.133	* 7	Zn(1′)I O(3′)I	2.001	* 7
O(2′) O(3′)	3.347	*38	O(1) O(1′)	2.706	*38
O(2′) O(4′)	3.022	*30	O(1) O(2′)	3.081	*32
O(2′) O(6′)	2.954	*31	O(1) O(3′)	3.405	*38
O(3′) O(4′)	3.431	*38	O(1′) O(2′)	3.479	*37
O(3′) O(6′)	3.489	*35	O(1′) O(3′)	3.013	*38
O(4′) O(6′)	3.289	*31	O(2′) O(3′)	3.264	*35
Zn(2′) O	2.02	* 7	Zn(1′) O	1.95	* 7
O O	3.25	*34	O O	3.25	*36

Table 4. *(Continued)*

Triangle I			Triangle II		
B(1)I—O(1)I	1.236	*44 Å	B(2)B—O(4)I	1.291	*51 Å
B(1)I O(2)I	1.403	*44	B(2)B O(5)B	1.448	*51
B(1)I O(3)I	1.483	*44	B(2)B O(6)G	1.537	*51
O(1) O(2)	2.357	*39	O(4) O(5)	2.413	*53
O(1) O(3)	2.331	*36	O(4) O(6)	2.506	*34
O(2) O(3)	2.439	*46	O(5) O(6)	2.474	*43
B(1) O	1.37	*44	B(2) O	1.43	*51
O O	2.38	*40	O O	2.46	*43
Triangle III			Triangle IV		
B(2′)I—O(4′)I	1.424	*47	B(1′)I—O(1′)I	1.345	*50
B(2′)I O(5′)I	1.337	*47	B(1′)I O(2′)B	1.472	*50
B(2′)I O(6′)A	1.215	*47	B(1′)I O(3′)I	1.242	*50
O(4′) O(5′)	2.279	*30	O(1′) O(2′)	2.415	*38
O(4′) O(6′)	2.282	*31	O(1′) O(3′)	2.357	*38
O(5′) O(6′)	2.304	*52	O(2′) O(3′)	2.231	*35
B(2′) O	1.32	*47	B(1′) O	1.35	*50
O O	2.29	*38	O O	2.34	*37

* Estimated standard deviations, multiplied by 0.001. At the end of each tetrahedron or triangle the mean value is given.

The crystal structure of $Zn_3(BO_3)_2$ contains ribbons of $(BO_3)^{3-}$ triangles which share a common vertex with $(ZnO_4)^{6-}$ tetrahedra, these tetrahedra sharing common vertices and edges (Fig. 5). Some

Table 5. *Valence angles in tetrahedra and triangles*

Tetrahedron I			Tetrahedron II		
O(2)—Zn(1)—O(3)	116.36°	*1.33°	O(2)—Zn(2)—O(3)	110.10°	*1.30°
O(1)—Zn(1)—O(2)	130.05	1.12	O(3)—Zn(2)—O(6)	119.59	1.23
O(3)—Zn(1)—O(1′)	113.86	1.28	O(4)—Zn(2)—O(6)	107.02	1.19
O(1)—Zn(1)—O(1′)	81.95	1.05	O(6)—Zn(2)—O(2)	99.11	1.27
O(1)—Zn(1)—O(3)	102.46	1.23	O(3)—Zn(2)—O(4)	119.53	1.24
O(2)—Zn(1)—O(1′)	107.36	1.15	O(2)—Zn(2)—O(4)	99.15	1.21
Tetrahedron III			Tetrahedron IV		
O(4)—Zn(3)—O(5)	115.19	1.37	O(5)—Zn(3′)—O(5′)	110.07	1.48
O(5)—Zn(3)—O(6)	94.47	1.46	O(5′)—Zn(3′)—O(4′)	112.33	1.22
O(6)—Zn(3)—O(5′)	101.81	1.41	O(4′)—Zn(3′)—O(6′)	118.24	0.92
O(4)—Zn(3)—O(5′)	113.28	1.31	O(5)—Zn(3′)—O(6′)	101.76	1.25
O(5)—Zn(3)—O(5′)	107.35	1.35	O(5)—Zn(3′)—O(4′)	108.19	1.17
O(4)—Zn(3)—O(6)	122.27	1.43	O(5′)—Zn(3′)—O(6′)	105.66	1.32

* Estimated standard deviations

Table 5. *(Continued)*

Tetrahedran V			Tetrahedron VI		
O(4′)—Zn(2′)—O(6′)	106.65°	*0.88°	O(3′)—Zn(1′)—O(2′)	112.17°	*1.08°
O(6′)—Zn(2′)—O(3′)	118.93	1.02	O(2′)—Zn(1′)—O(1′)	131.02	1.13
O(3′)—Zn(2′)—O(2′)	113.68	1.07	O(1′)—Zn(1′)—O(1)	88.97	1.07
O(2′)—Zn(2′)—O(4′)	96.58	0.94	O(1)—Zn(1′)—O(3′)	118.09	1.03
O(2′)—Zn(2′)—O(6′)	89.00	0.91	O(1)—Zn(1′)—O(2′)	104.33	1.11
O(4′)—Zn(2′)—O(3′)	124.21	1.12	O(1′)—Zn(1′)—O(3′)	101.38	1.06
Triangle I			Triangle II		
O(1)—B(1)—O(2)	126.44	2.90	O(6)—B(2)—O(4)	124.59	3.06
O(2)—B(1)—O(3)	115.35	2.68	O(4)—B(2)—O(5)	123.46	3.25
O(3)—B(1)—O(1)	117.76	2.84	O(5)—B(2)—O(6)	111.90	2.97
O(1)—O(2)—O(3)	58.13	1.18	O(6)—O(4)—O(5)	60.34	1.26
O(2)—O(3)—O(1)	59.17	1.19	O(4)—O(5)—O(6)	61.69	1.28
O(3)—O(1)—O(2)	62.70	1.24	O(5)—O(6)—O(4)	57.96	1.23
Triangle III			Triangle IV		
O(5′)—B(2′)—O(4′)	111.22	2.88	O(3′)—B(1′)—O(2′)	110.30	2.91
O(4′)—B(2′)—O(6′)	119.51	2.83	O(2′)—B(1′)—O(1′)	118.02	2.88
O(6′)—B(2′)—O(5′)	129.04	3.27	O(1′)—B(1′)—O(3′)	131.29	3.31
O(5′)—O(4′)—O(6′)	60.68	1.20	O(3′)—O(2′)—O(1′)	60.80	1.13
O(4′)—O(6′)—O(5′)	59.59	1.18	O(2′)—O(1′)—O(3′)	55.72	1.07
O(6′)—O(5′)—O(4′)	59.72	1.19	O(1′)—O(3′)—O(2′)	63.47	1.15

Table 6

Compounds	Triangles		Tetrahedra		Reference
	B—O	O—O	X—O	O—O	
Kotoite	1.32—1.42	2.33—2.38			Berger (1949)
Fluoborite	1.50	2.45			Takéuchi (1950)
Warwickite	1.30—1.45	2.32—2.45			Takéuchi *et al.* (1950)
Ludwigite	1.40—1.50	2.40—2.50			
Pinakiolite	1.27—1.50	2.38—2.48			
Vonsenite	1.39	2.40			Takéuchi (1956)
Hambergite	1.28—1.42	2.31—2.39	1.75—1.81 1.56—1.74	2.52—2.73 2.48—2.75	Zachariasen (1931)
α $Zn_3(PO_4)_2$			1.93—2.03 1.86—2.03	3.21—3.26 3.06—3.23	Calvo (1965)
γ $Zn_3(PO_4)_2$			1.98—2.16		Calvo (1963)

of these tetrahedra are regular ones sharing common vertices while the rest are distorted ones sharing common edges. Every chain of tetrahedra is built up of a sequence of six tetrahedra sharing a common vertex and two tetrahedra sharing a common edge. The tetrahedra along a chain sharing common vertices are also connected to those of adjacent chains through vertices. However the tetrahedra in a chain sharing a common edge are connected to those of adjacent tetrahedra through the triangle sides of $(BO_3)^{3-}$.

This atomic array accounts for the good {100} cleavage in $Zn_3(BO_3)_2$ and for the preferred orientation observed in powder diffractograms for the reflections $h00$.

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