Acta Cryst. (1964). **17**, 749

The Crystal Structure of Lithium Metaborate

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(*Received* 19 *July* 1963)

Lithium metaborate, $LiBO_2$, is monoclinic, space group $P2_1/c$, with four molecules in a cell of dimensions $a=5{\cdot}838$, $b=4{\cdot}348$, $c=6{\cdot}449$ Å, $\beta=115{\cdot}12°$, and all atoms in general positions.

Refinement of the structure gave $R=0{\cdot}046$ and a precision of 0·008 Å for Li–O, 0·006 Å for B–O bonds.

The structure contains endless chains of BO_3 triangles with Li–O bonds between chains.

Introduction

The investigation reported in this paper is part of a systematic study of borate structures being carried on in this laboratory.

Lithium metaborate, $LiBO_2$, was prepared from the melt, orthoboric acid and lithium carbonate serving as starting materials. A fibrous mass of monoclinic needles of the metaborate was obtained on cooling the melt. The needles are flat, (001) being the prominent face and the crystallographic **b** direction the needle axis. Twins are very common. The twinning plane is (100), so that the two individuals have a common [001] zone.

A direct determination gave a density of 2·18 g.cm^{-3}.

The primitive monoclinic cell contains four molecules $LiBO_2$ and has dimensions

$$a=5{\cdot}838\pm0{\cdot}002,\ b=4{\cdot}348\pm0{\cdot}001,\ c=6{\cdot}449\pm0{\cdot}002\ \text{Å}$$
$$\beta=115{\cdot}12\pm0{\cdot}02°.$$

The calculated density is 2·223 g.cm^{-3}.

Reflections $H0L$ are absent for odd L, and reflections $0K0$ for odd K. Hence, the suggested space group symmetry is $P2_1/c$.

Determination of the structure

Precise intensity measurements were made with a single-crystal spectrometer, a proportional counter and Cu $K\alpha$ radiation. The crystal specimens were so small that absorption effects were entirely negligible.

The intensities of all reflections $H0L$, $H1L$, $0KL$ and $1KL$ were measured. Because of the simplicity of the structure, adequate precision was obtained with this limited set of data, consisting of 198 distinct reflections.

Standard methods of structure determination showed all atoms to be in general space group positions, $\pm(xyz)(x,\frac{1}{2}-y,\frac{1}{2}+z)$, and gave approximate values for the twelve position parameters.

The least-square refinements (using the Busing–Levi IBM 704 program) assumed anisotropic thermal motion and the f curves for neutral atoms given in *International Tables for X-Ray Crystallography*. All experimental F values were given unit weight.

A small correction for secondary extinction was applied in accordance with the proper formula (Zachariasen, 1963*a*). The correction amounted to less than five per cent except for the following experimental F values: 002 (24%), $10\bar{2}$ (18%), 020 (11%) and $10\bar{4}$ (9%).

The ultimate refinement gave a conventional R index of 0·046 including, 0·041 omitting 'zeros'. The results as to positional and thermal parameters are given in Tables 1 and 2, while Tables 3 and 4 list observed and calculated structure factors.

Table 1. *Position parameters* ($\times10^4$)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Li	4322	12	2131	21	3437	11
B	1233	9	6735	14	2720	7
O(1)	0846	5	3550	8	2592	5
O(2)	3548	5	7741	8	3169	4

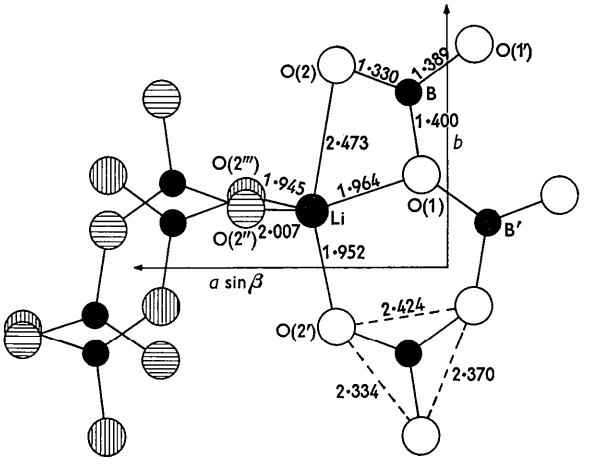

Fig. 1. The structure viewed along the c axis. Only three of the four BO_2 chains per cell are shown. Unshaded oxygen atoms indicate the chain lying approximately in the projection plane, shaded oxygen atoms chains at heights $\pm c/4$ above and below the plane.

Table 2. *Anisotropic thermal parameters* ($\times 10^4$)

	Li	σ	B	σ	O(1)	σ	O(2)	σ
β_{11}	121	21	97	15	92	10	83	9
β_{22}	213	42	130	30	80	17	139	19
β_{33}	164	18	91	10	177	8	118	7
β_{12}	19	51	8	41	−12	25	−20	20
β_{13}	74	17	45	10	67	7	55	7
β_{23}	−9	27	−6	15	12	10	−2	10

The structure

The structure contains endless chains of BO_3 triangles, with the b axis as the chain direction. The atoms of a chain are very nearly coplanar, parallel to $(10\bar{5})$, and also the lithium atoms lie approximately in the same layer. A lithium atom forms three Li–O bonds within one chain and one bond with each of two neighboring

Table 3. *Structure factors* H0L and H1L*

H0L	F_o	KF_c	*H0L*	F_o	KF_c	*H1L*	F_o	KF_c	*H1L*	F_o	FK_c
100	11·9	12·9	502	3·83	3·80	113	9·9	−9·9	41$\bar{6}$	3·16	2·94
10$\bar{2}$	41·6	−40·3	600	4·41	−4·64	21$\bar{4}$	2·68	2·27	016	6·2	−6·0
002	53·5	−55·6	60$\bar{6}$	6·7	7·0	11$\bar{4}$	3·70	3·61	61$\bar{3}$	1·52	−1·28
200	11·9	11·9	70$\bar{4}$	4·60	−4·76	311	8·0	7·7	511	0	0·48
20$\bar{2}$	8·1	7·2	404	6·9	−6·9	31$\bar{4}$	13·1	−13·0	61$\bar{2}$	6·0	6·1
102	4·93	4·34	70$\bar{2}$	5·7	5·9	014	10·1	9·7	61$\bar{4}$	12·5	−12·5
30$\bar{2}$	20·7	−19·4	206	0	0	41$\bar{2}$	6·4	−6·5	314	4·37	4·10
300	9·3	9·0	30$\bar{8}$	3·81	−3·24	41$\bar{1}$	6·8	−6·5	51$\bar{6}$	3·33	−3·25
202	17·3	−17·2	40$\bar{8}$	3·43	3·17	41$\bar{3}$	6·1	6·0	215	3·81	3·87
20$\bar{4}$	7·2	−5·7	208	9·1	8·8	213	8·5	−8·4	61$\bar{1}$	2·40	2·24
10$\bar{4}$	36·8	36·7				410	2·57	2·69	413	2·36	−2·37
30$\bar{4}$	9·5	9·5				21$\bar{5}$	4·34	−4·07	31$\bar{7}$	5·4	5·3
004	12·6	12·3	*H1L*	F_o	KF_c	41$\bar{4}$	1·16	0·91	21$\bar{7}$	1·32	1·34
40$\bar{2}$	20·8	20·5				312	4·33	−4·23	61$\bar{5}$	0	−0·19
400	26·0	−26·7	011	0·99	−0·76	114	2·79	−3·05	41$\bar{7}$	4·39	4·66
40$\bar{4}$	4·78	−4·64	110	16·0	17·7	11$\bar{5}$	1·47	−1·39	116	4·33	3·94
302	7·5	7·4	11$\bar{1}$	5·2	−5·7	31$\bar{5}$	10·1	−10·1	11$\bar{7}$	0	0·76
104	2·08	2·12	111	10·1	10·7	411	5·0	5·0	512	9·5	9·6
50$\bar{2}$	16·2	16·0	11$\bar{2}$	13·1	−13·2	015	1·55	1·75	610	2·44	2·58
50$\bar{4}$	20·7	−20·6	012	10·8	−10·9	51$\bar{2}$	13·5	13·2	61$\bar{6}$	9·7	9·7
204	7·8	7·5	21$\bar{1}$	20·7	−20·8	51$\bar{3}$	3·92	3·99	51$\bar{7}$	1·67	1·80
20$\bar{6}$	4·92	−5·05	210	25·3	−24·2	41$\bar{5}$	5·1	−5·2	017	2·21	−2·46
30$\bar{6}$	2·04	1·90	21$\bar{2}$	9·0	8·7	51$\bar{1}$	2·54	−2·60	71$\bar{3}$	3·68	−3·53
500	9·1	−9·3	112	3·65	−3·58	51$\bar{4}$	2·12	−2·16	71$\bar{4}$	5·2	5·6
402	14·6	14·6	11$\bar{3}$	1·84	1·69	214	5·5	−5·3	315	2·32	2·37
10$\bar{6}$	20·3	−19·6	211	17·1	16·9	313	4·53	−4·49	414	9·3	−9·3
40$\bar{6}$	4·41	−4·41	21$\bar{3}$	12·7	12·1	21$\bar{6}$	3·89	−3·97	611	2·36	−2·40
006	0·78	−0·62	013	0	0·32	31$\bar{6}$	3·67	3·86	71$\bar{2}$	4·70	−5·3
60$\bar{2}$	4·21	3·94	31$\bar{1}$	13·2	−12·6	510	18·6	−18·8	715	2·99	3·11
60$\bar{4}$	4·27	−4·28	31$\bar{2}$	18·4	17·6	115	6·3	6·3	216	1·52	−1·68
304	10·1	−10·0	310	7·7	−7·4	412	6·6	6·6	31$\bar{8}$	0	0·33
50$\bar{6}$	15·2	15·6	31$\bar{3}$	14·2	14·0	11$\bar{6}$	1·10	1·21			
106	5·0	−4·72	212	16·8	17·0	51$\bar{5}$	3·10	−3·15			

* In Tables 3 and 4, $K = 1{\cdot}198 \pm 0{\cdot}013$ for reflections $HK0$, while $K = 1{\cdot}065 \pm 0{\cdot}007$ for all other reflections.

Table 4. *Structure factors, 0KL and 1KL*

0KL	F_o	KF_c	*0KL*	F_o	KF_c	*1KL*	F_o	KF_c	*1KL*	F_o	KF_c
020	42·2	−41·2	051	2·52	−2·51	131	9·5	−9·2	13$\bar{5}$	1·54	1·89
021	15·5	14·6	052	2·05	−2·15	13$\bar{2}$	9·3	9·1	125	1·65	1·59
022	21·5	21·0	036	3·95	3·83	123	2·98	−3·19	12$\bar{6}$	10·4	10·8
023	8·1	−8·5	045	0	0·73	12$\bar{4}$	14·1	−17·9	14$\bar{3}$	2·14	−2·11
031	2·24	2·39	053	4·00	4·13	132	6·3	5·8	14$\bar{4}$	3·40	−1·25
032	5·3	5·4	027	0	−0·31	13$\bar{3}$	0	0·13	150	4·93	4·85
024	1·50	−1·75				124	2·70	2·44	15$\bar{1}$	4·55	4·22
033	2·28	−2·48				12$\bar{5}$	3·40	−3·51	135	11·0	−9·9
040	0	−1·23	1*KL*	F_o	KF_c	133	12·5	12·9	13$\bar{6}$	0	−0·16
041	1·45	−1·67	120	9·4	9·6	13$\bar{4}$	3·50	−3·86	151	0	0·04
025	3·11	2·95	12$\bar{1}$	11·6	−11·1	140	16·1	−16·4	15$\bar{2}$	4·50	−4·47
034	5·6	−6·3	121	8·6	8·1	14$\bar{1}$	0	0·15	144	6·8	−6·1
042	3·41	3·98	12$\bar{2}$	11·4	11·0	141	1·24	1·03	126	2·55	2·26
043	0	0·91	122	11·7	−11·9	14$\bar{2}$	6·9	7·5	14$\bar{5}$	0	0·07
035	1·51	−1·68	12$\bar{3}$	7·6	7·9	142	13·3	13·3	12$\bar{7}$	1·40	1·39
026	3·56	−3·08	130	12·2	−12·1	14$\bar{3}$	0	−0·04	152	1·62	−1·64
044	7·5	−7·5	13$\bar{1}$	1·66	1·54	134	0	−0·02	15$\bar{3}$	3·40	−3·26

Table 5. *Heat motion data*

Atom	i	Δi	Angles a	Angles b	Angles c	Direction cosines α	Direction cosines β	Direction cosines γ
Li	1	0·117 ± 0·023 Å	156° ± 33°	66° ± 33°	67° ± 11°	0·91	−0·41	0
	2	0·147 ± 0·020	66 ± 33	26 ± 34	90 ± 26	0·41	0·90	0·16
	3	0·169 ± 0·010	86 ± 14	80 ± 26	157 ± 11	−0·07	−0·17	0·98
B	1	0·106 ± 0·024	128 ± 39	40 ± 36	64 ± 24	−0·62	0·77	0·18
	2	0·119 ± 0·023	38 ± 38	53 ± 37	103 ± 60	0·79	0·60	0·13
	3	0·126 ± 0·007	91 ± 50	77 ± 41	151 ± 35	0·02	−0·23	0·97
O(1)	1	0·081 ± 0·017	114 ± 23	156 ± 23	80 ± 6	0·41	0·91	0
	2	0·111 ± 0·011	25 ± 22	113 ± 23	103 ± 6	0·91	−0·39	0·16
	3	0·177 ± 0·004	81 ± 4	95 ± 3	163 ± 3	−0·16	0·09	0·98
O(2)	1	0·093 ± 0·012	152 ± 16	118 ± 16	69 ± 6	0·88	0·47	0
	2	0·121 ± 0·010	118 ± 16	28 ± 16	77 ± 13	−0·47	0·88	0
	3	0·143 ± 0·005	90 ± 7	88 ± 12	155 ± 7	0	−0·04	1·00

chains as illustrated in Fig. 1 which views the structure along the c axis.

The standard errors are ±0·008 Å for Li–O bonds, ±0·006 Å for B–O bonds and ±0·004 Å for O–O separations. Individual interatomic distances are (see Fig. 1):

B–O(1)	= 1·400 Å	Li–O(1)	= 1·964 Å
B–O(1′)	= 1·389 Å	Li–O(2)	= 2·473 Å
B–O(2)	= 1·330 Å	Li–O(2′)	= 1·952 Å
O(1)–O(1′)	= 2·370 Å	Li–O(2″)	= 2·007 Å
O(1)–O(2)	= 2·334 Å	Li–O(2‴)	= 1·945 Å
O(1′)–O(2)	= 2·424 Å		

and the bond angle B–O(1)–B′ is 132·8°.

One edge of the BO_3 triangle is shared with the oxygen polyhedron about lithium. As a consequence of lithium–boron repulsion (Li–B = 2·601 Å) this triangle edge is unusually short and the Li–O(2) bond is exceptionally long.

An O(1) atom is bonded to two boron and one lithium atom and is thus 'overbonded'. The O(2) atom, forming one O–B bond and four O–Li bond is correspondingly 'underbonded'. This binding imbalance is partly compensated for by a weakening (*i.e.* lengthening) of the B–O(1) bonds and by a strengthening of the B–O(2) bond (see the discussion in Zachariasen, 1963*b*).

The endless chain $[BO_2]_\infty^{-\infty}$ was first observed in CaB_2O_4 (Zachariasen, 1931; Zachariasen & Ziegler 1932; Marezio, Plettinger & Zachariasen, 1963*a*). However, in the alkali borates, KBO_2 (Zachariasen, 1937) and $NaBO_2$ (Fang 1938; Marezio, Plettinger & Zachariasen, 1963*b*) there are insular groups $[B_3O_6]^{-3}$.

The hydrate, $LiBO_2.8H_2O$, is trigonal with space group $C3$ and one molecule in a cell of dimensions $a = 6{\cdot}555$, $c = 6{\cdot}177$ Å. The structure of this compound, to be reported in a forthcoming paper, contains complexes $[B(OH)_4]^-$ and $[Li(OH_2)_4]^+$ held together by hydrogen bonds.

The refractive indices of $LiBO_2$ have not been measured. According to the structure the birefringence should be strong with the vibration direction α normal to the $(10\bar{5})$ plane.

The fibrous character of the crystals with b the fiber axis is due to the presence of the $[BO_2]_\infty^{-\infty}$ chains and to weak cohesive forces along [100] and [001]. Similarly the observed twinning is explained by the fact that the normal to the (100) plane is a pseudo-twofold axis.

The heat motion

In Table 5 are given the root mean square amplitudes, Δ_i, along the principal axes, the angles between the principal axes and the vectors **a**, **b**, **c**. The quantities α, β, γ are the direction cosines of the principal axes in a cartesian system, $X||\mathbf{a}, Y||\mathbf{b}, Z||\mathbf{a}\times\mathbf{b}$.

The direction cosines for the normal to the BO_3 triangle in this reference frame are: −0·203, 0, 0·979. The maximum thermal displacements of all atoms are thus within experimental error normal to the $(10\bar{5})$ plane.

The writer is indebted to Miss H. A. Plettinger, who made many of the intensity measurements, and to the Applied Mathematics Division of Argonne National Laboratory for the use of the IBM 704 computer. The support of the Advanced Research Projects Agency is gratefully acknowledged.

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