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The Crystal Structure of Lithium Diborate, $Li_2O.2B_2O_3$

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Single crystals of lithium diborate, $Li_2O.2B_2O_3$, have been synthesized and the crystal structure determined. The crystals belong to the space group $I4_1cd$, with unit-cell dimensions:

$$a = 9{\cdot}47 \text{ Å},\ c = 10{\cdot}26 \text{ Å} .$$

An approximate set of atomic parameters was determined by trial-and-error methods, and the parameters were refined by calculating electron-density projections. The result shows that the borate anion consists of two three-dimensional interlocking networks, extending throughout the crystal. The basic unit of the networks is a group consisting of two boron atoms tetrahedrally coordinated by oxygen and two boron atoms triangularly coordinated by oxygen. The atoms in the group are arranged as a twisted double ring. This group is similar to one found as an isolated ion in borax, $Na_2O.2B_2O_3.10H_2O$. Half of the boron atoms in lithium diborate are four-fold coordinated. This is shown to be consistent with a relationship valid for most borate structures. Two exceptions to this relationship are discussed.

Introduction

It has often been suggested that the anhydrous alkali polyborates form a series of structures in a manner analogous to the well known silicate structures. Since a chain structure is known to occur in calcium metaborate, $CaO.B_2O_3$ (Zachariasen & Ziegler, 1932), it has been proposed by several workers that a corresponding double chain occurs in diborates such as dehydrated borax. (See for instance Azaroff, 1960, p. 425). This situation would be analogous to the condensation of the single chains in the pyroxenes to the double chains in the amphiboles. As the present crystal-structure determination shows, however, the anhydrous borates behave differently.

During the last years the crystal structures of a number of hydrated polyborates have been determined, and some general structural principles have been pointed out (Pauling, 1960; Edwards & Ross, 1960; Dale, 1961). It has been suggested that most of the principles applicable to the hydrated borates are also valid to a large extent for the anhydrous borates (Krogh-Moe, 1960*a*). The main difference between a hydrated borate and the same compound in a dehydrated state is that two B–O–H groups in the former phase have reacted to form a B–O–B bridge in the latter phase. Thus the isolated polyions, which are found in a sufficiently hydrated compound, are induced to share 'corners' with each other, thereby becoming units of an infinite three-dimensional network in the anhydrous compound.

To establish the above structural picture of the anhydrous polyborates, a series of crystal structure investigations has been undertaken. Previously in this series, the structures of potassium pentaborate, $K_2O.5B_2O_3$ (Krogh-Moe, 1959), and cesium triborate, $Cs_2O.3B_2O_3$ (Krogh-Moe, 1960*b*), have been determined. The present work is concerned with the structure of lithium diborate, $Li_2O.2B_2O_3$.

Experimental

Crystalline lithium diborate occurs as a congruently melting phase in the system lithium oxide–boron oxide (Sastry & Hummel, 1958). The melting point is 917 °C. Small single crystals were prepared in a platinum crucible by fusing the calculated amounts of lithium carbonate with boric acid to a glass and subjecting the glass to a further heat treatment between 800 and 900 °C.

The unit-cell dimensions and space group were determined from Weissenberg photographs. Equatorial and non-equatorial layers around the a and c axis of the tetragonal cell were recorded, using the Cu $K\alpha$ wavelength. The unit-cell dimensions were found to be

$$a = b = 9{\cdot}47,\ c = 10{\cdot}26 \text{ Å} .$$

With 8 formula units of $Li_2O.2B_2O_3$ in the cell, this gives a calculated density of 2·44 $g.cm.^{-3}$. The symmetry and systematic extinctions settle the space group uniquely as $I4_1cd$. (A couple of relatively weak spots with the forbidden indices 110 and 101 were observed, however, but they did not recur symmetrically at $1\bar{1}0$ and $10\bar{1}$. By this lack of symmetry, the two reflections stand apart from all the others; moreover their intensity relative to the others seems to vary from one crystal to another. No further attention was given to this phenomenon.)

Cu $K\alpha$-radiation and the multiple-film technique were used to take integrated equatorial Weissenberg photographs about the a and c axis. The crystals had

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	$\lvert F_c \rvert$
200	34	+30	004	90	103
400	55	−59	008	46	58
600	52	+50	0,0,12	63	68
800	34	−39	202	76	78
10,0,0	33	−30	204	29	14
310	6	−5	206	37	32
510	22	+15	208	22	16
710	42	−39	2,0,10	31	25
910	32	+34	2,0,12	22	20
220	9	−12	402	46	37
420	35	+34	404	58	58
620	70	+76	406	75	71
820	17	+18	408	41	26
10,2,0	26	+26	4,0,10	30	18
530	33	−24	4,0,12	13	9
730	30	+28	602	17	16
930	8	−4	604	25	13
440	6	0	606	69	58
640	46	+41	608	24	26
840	59	+65	6,0,10	46	43
10,4,0	23	+26	802	10	2
750	7	−1	804	76	84
950	15	−19	806	52	54
660	42	−39	808	46	38
860	7	−12	10,0,2	31	32
			10,0,4	29	35
			10,0,6	16	10

quadratic cross-sections perpendicular to the axis of rotation, with side lengths about 0·01 cm. The relative intensities were estimated visually by comparison with a calibrated scale, and the usual corrections for Lorentz and polarization factors were made. The structure factors obtained from the experimental intensities are listed in Table 1 under the heading F_o.

Structure analysis

The general positions in the space group $I4_1cd$ are sixteen-fold. If we place on lithium atom, two boron atoms and three oxygen atoms in different general positions, we are left with one oxygen atom which has to be placed in a special eight-fold position with parameter values 0, 0, z. Based on a Patterson projection along the c-axis, trial positions for the four non-equivalent oxygen atoms were obtained. The structure has a center of symmetry in this particular projection, and the best trial structures gave a sufficient number of reliable signs to permit the calculation of an electron-density map. There is a considerable overlap of atoms in the projection, but reasonably good values for the x and y parameters were subsequently obtained by calculating electron-density maps where the contributions from one or several atoms were subtracted. The projection was refined until a discrepancy index of $R(hk0) = 12{\cdot}8\%$ was obtained. The calculated structure factors, $F_c(hk0)$, are given in Table 1. They are based on the Hartree scattering factors and a temperature factor $B = 0{\cdot}6\ \text{Å}^2$.

Preliminary z parameters were derived by making use of the observed boron–oxygen distances in the x–y projection together with the known boron–oxygen bond lengths. Phase angles could then be calculated for the structure factors of the non-centrosymmetric x–z projection. With the aid of electron-density maps this projection was refined until a discrepancy index $R(h0l) = 14{\cdot}8\%$ was reached. The absolute values of the calculated structure factors, $F_c(h0l)$, for this projection are given in Table 1. ($F(h00)$ values are given with signs.) The same temperature factor $B = 0{\cdot}6\ \text{Å}^2$, was again applied.

Table 2. *Positional parameters*

Atom	x/a	y/b	z/c
$\mathrm{O_{I}}$	0·135	0·283	0·260
$\mathrm{O_{II}}$	0·179	0·067	0·150
$\mathrm{O_{III}}$	−0·060	0·157	0·171
$\mathrm{O_{IV}}$	0·000	0·000	0·000
$\mathrm{B_{I}}$	0·081	0·169	0·194
$\mathrm{B_{II}}$	0·115	−0·054	0·083
Li	0·158	0·158	0·860

Table 2 gives the final atomic parameters. The oxygen atom, denoted $\mathrm{O_{IV}}$ in the table, occupies a special eight-fold position. The other six atoms occupy general sixteen-fold positions.

Discussion of the structure

The basic structural unit of the borate network, as viewed along the a-axis, is shown in Fig. 1. It consists of two non-planar six-membered rings combined in one group. Two boron atoms and one oxygen atom of the group belong simultaneously to both rings. The group is somewhat twisted, and therefore has no true mirror-plane symmetry.

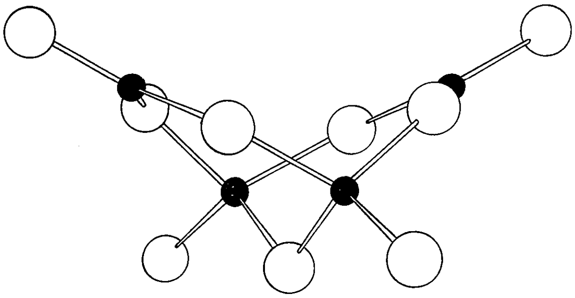


Fig. 1. The basic structural unit of the borate networks in lithium diborate, as viewed along the a-axis. The smaller, black spheres represent boron atoms, the larger, open spheres represent oxygen atoms.

A similar unit has been found as an isolated ion in borax (Morimoto, 1956). In the structure of borax the four oxygen atoms, which are shown as linked to only one boron atom in Fig. 1, are presumably hydroxyl groups. In the lithium diborate structure, however, these four oxygen atoms act as bridges between identical units, thereby forming an infinite three-dimensional network. Actually the structure consists of two such network which are separate and interlocking. The arrangement of these networks can be seen from Fig. 2, which shows a projection along the c-axis. The figure gives a small arbitrary section of both networks.

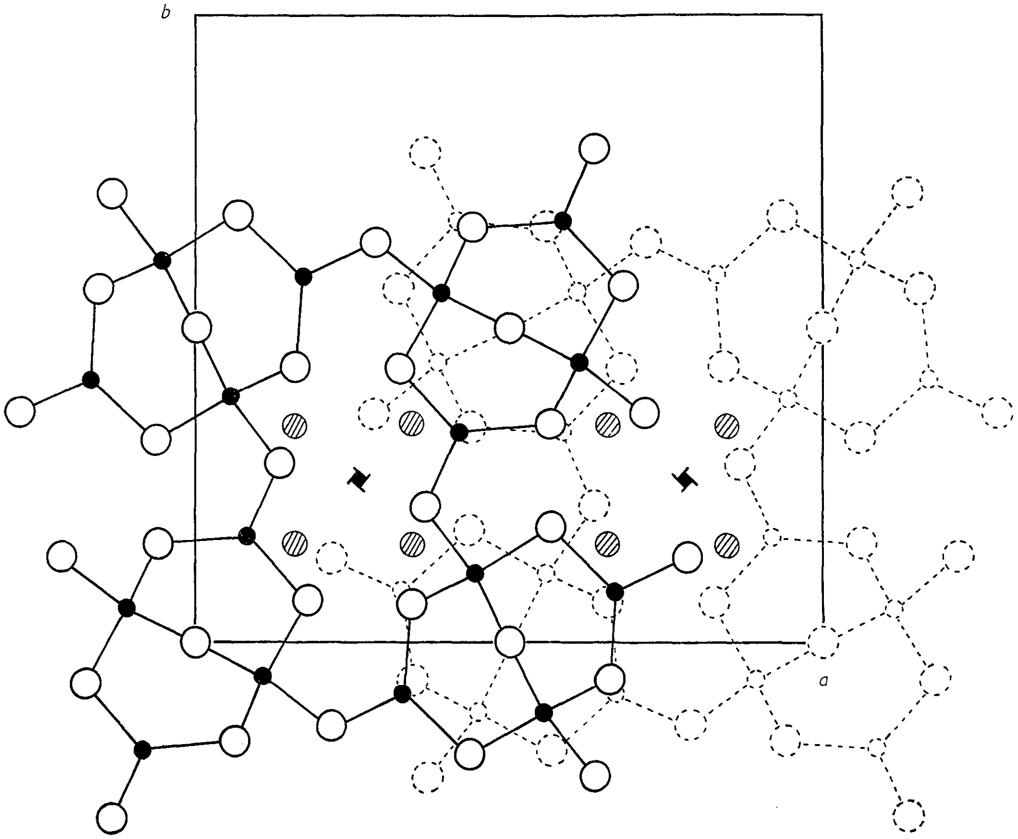


Fig. 2. A projection of the structure along the *c*-axis, showing the manner in which the structural units are interlinked to a three-dimensional network. Only a small section of the network is shown. Black spheres represent boron atoms, open spheres represent oxygen atoms, and shaded spheres represent lithium atoms. The broken lines indicate part of a second network, which is a separate, interlocking twin to the first network. The unit cell dimensions are indicated by the large square.

(One of the twin networks is drawn with dashed lines. The projection of each network is made for partly different regions of the unit cell to avoid complicating the figure by overlap of the networks).

The closest boron–oxygen and oxygen–oxygen distances in the structure are, within the limits of error, equal to those found in several other comparable borate structures (Clark, 1959). Values for the boron–oxygen distances calculated from the parameters in Table 2 are listed in Table 3. The average boron–oxygen distance in the tetrahedron is 1·45 Å and the corresponding average distance found for the triangle is 1·39 Å.

Table 3. *Interatomic distances*

B_I–O_I	1·38 Å	O_I'–O_{IV}	2·42 Å
B_I–O_{II}	1·42	O_{II}–O_{IV}	2·38
B_I–O_{III}	1·37	O_{III}–O_{IV}	2·37
B_{II}–O_{IV}	1·47	O_I'–O_{III}	2·23
B_{II}–O_{III}	1·43	O_{II}–O_{III}	2·41
B_{II}–O_{II}	1·46	O_I'–O_{II}	2·40
B_{II}–O_I'	1·44	O_I–O_{III}	2·38
		O_I–O_{II}	2·38
		O_{II}–O_{III}	2·44

The lithium position, shown as a shaded circle in Fig. 2, is less accurately determined. Because of the low X-ray scattering power of the lithium atom and because of partial overlap by other atoms, the lithium parameters could not be obtained with high precision from the electron-density projections. Limited significance should therefore be given to the lithium–oxygen distances obtainable from the present data. None of these distances, however, is less than 2·1 Å.

The coordination numbers of boron

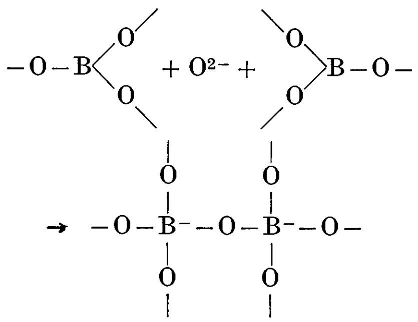
The formula for a metal polyborate may be written in a general manner as follows:

$$xMe_2O\,.\,(100-x)B_2O_3\,.\,yH_2O\ .$$

By limiting ourselves to compounds where x is not larger than 50, it is possible (with a couple of exceptions) to determine the fraction of boron atoms in regular tetrahedral coordination, N_{BO_4}, from the following equation:

$$N_{BO_4}=x/(100-x)\ . \qquad (1)$$

A graphical plot of this equation is given as Fig. 4 in a recent paper by Krogh-Moe (1960*b*). The above equation is based upon a definite reaction scheme of an oxide with a borate network:


(2)

This is an oxide counterpart to the well known reaction of boron fluoride with a fluoride ion:

$$BF_3 + F^- \rightarrow BF_4^- . \qquad (3)$$

In these reactions the boron atom in a triangular sp^2 hybrid quantum state collects an additional electron to adopt the tetrahedral sp^3 hybrid quantum state.

Equation (1) shows that the water content has no effect on the coordination number of boron. Actually water does not promote a coordination change, because it attacks the borate network by opening already existing B–O–B linkages:

$$>B\text{–}O\text{–}B< + H_2O \rightarrow\ >B\text{–}O\text{–}H \quad H\text{–}O\text{–}B< . \qquad (4)$$

If water, on the other hand, were to behave like an alkali oxide (i.e. react according to 2), there would not be any non-bridging oxygens in the structure, with which the hydrogen ion could form strong hydroxyl bonds.

Several authors have quoted experimental evidence that the number of boron atoms in four-fold coordination in a hydrated crystalline borate is equal to the number of cation charges (Pauling, 1960; Edwards & Ross, 1960; Dale, 1961). This statement, of course, implies equation (1). Since the water content does not seem to influence the coordination numbers of boron, equation (1) is presumably valid also for the anhydrous borates. In support of this, the lithium diborate structure reported in this paper can be mentioned. Here we have $x = 33\frac{1}{3}$, giving the observed value of N_{BO_4} equal to 0·5. The equation is also obeyed by potassium pentaborate (Krogh-Moe, 1959) and cesium triborate (Krogh-Moe, 1960*b*).

The ordinary anhydrous metaborates, however, are notable exceptions to equation (1). With an x-value of 50, they ought to have all the boron atoms four-fold coordinated, whereas it is instead found experimentally that all the boron atoms are three-fold coordinated (Zachariasen, 1937; Zachariasen & Ziegler, 1932). Lithium metaborate ($LiBO_2$), however, does have a cristobalite type of modification (Lehman & Tiess, 1959), which consequently obeys equation (1). This modification becomes stable at relatively small pressures, but the cristobalite–quartz transition has not been observed up to 140 kb. (Dachille, 1960). These pressure data, together with the fact that all the boron atoms are four-fold coordinated in the hydrated metaborates (Edwards & Ross, 1960), suggests that the space requirements of the foreign cations may be responsible for the anomalous coordination behaviour of boron in the anhydrous metaborates. The calcium and potassium ions, for instance, are too large to enter a cristobalite type or related type of borate lattice in sufficient numbers. A three-fold coordination of boron is therefore preferred in this case.

If the above speculations are correct, one would expect that a four-fold coordination of boron in anhydrous metaborates can be promoted by lowering the concentration of foreign cations. This is actually done for calcium metaborate by substituting 50% of the $Ca(BO_2)_2$ groups with $(SiO_2)_2$ groups. The substitution leads to the mineral danburite, where all the boron atoms are known to be four-fold coordinated (Johansson, 1959).

Finally another exception to equation (1) should be mentioned. When $x = 0$, the equation requires that all the boron atoms are three-fold coordinated. This is true for crystalline boric acid and the orthorhombic modification of metaboric acid, but monoclinic metaboric acid has been reported to have one third of the borons in four-fold coordination (Zachariasen, 1952). The reason for this is somewhat obscure, though an attempt to 'explain' the structure has been made by Edwards & Ross (1960). Also crystalline boron oxide appears to violate equation (1) by being built up from irregular BO_4-tetrahedra (Berger, 1953). Presumably the boron atoms in these tetrahedra are not in a regular sp^3 hybrid quantum state. Therefore equation (1) may be extended also to this case provided that only borons in the sp^3 state are included when the boron atoms in tetrahedral coordination are counted. With this limitation, the fraction of boron atoms in four-fold coordination for the region of x from 0 to at least 33 can be determined from equation (1) even in the case of the anhydrous alkali borate glasses. (The proof for this will be given elsewhere.)

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