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The Crystal Structure of Cubic Metaboric Acid

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$\gamma-HBO_2$ is cubic with $a = 8{\cdot}886 \pm 0{\cdot}001$ Å and 24 molecules per unit cell. The space group is $P\bar{4}3n$. All atoms are in general positions with the following coordinates:

	x	y	z
H	0·937	0·103	0·337
B	0·2172	0·0816	0·3094
O_I	0·0804	0·1671	0·3004
O_{II}	0·3223	0·1447	0·4262

The boron and oxygen atoms form a three-dimensional network of BO_4 tetrahedra, the B–O bond lengths being 1·436, 1·465, 1·482 and 1·505 Å.

The hydrogen atom forms a strong bond $H–O_{II} = 1{\cdot}06$ Å and a weaker bond $H\ldots O_I = 1{\cdot}43$ Å with a length of 2·487 Å for the nearly linear group $O_{II}–H\ldots O_I$. However, the experimental data indicate appreciable resonance with the configuration $O_{II}\ldots H–O_I$.

A detailed study of the equilibrium diagram for the system $B_2O_3–H_2O$ was made by Kracek, Morey & Merwin (1938). These investigators showed that metaboric acid, HBO_2, can be prepared in three crystalline forms.

Approximate crystal structures have been reported for the orthorhombic α-HBO_2 (designated HBO_2–III by Kracek *et al.*) (Tazaki, 1940) and for the monoclinic β-HBO_2 (HBO_2–II) (Zachariasen, 1952). For the latter crystal a precise determination has since been carried out and will soon be reported by the writer.

The present paper describes the results of a detailed structural study of γ-HBO_2 (HBO_2–I).

Experimental procedure

The investigation was carried out using the original crystals supplied to the writer by Dr Kracek in 1936.

γ-HBO_2 is cubic with $a = 8{\cdot}886 \pm 0{\cdot}001$ Å and 24 stoichiometric molecules per unit cube. The measured and calculated density is 2·487 g.cm.$^{-3}$.

The crystals show holohedral Laue symmetry, and the only systematic absences are (HHL) for odd L. Hence the suggested space groups are $Pm3n$ and $P\bar{4}3n$.

The diffraction intensities were measured with high precision using a proportional counter and Cu $K\alpha$ radiation.

The measurements were made on two crystal specimens. Both of them were ground into precise spheres, the radii being 0·0105 cm. and 0·0188 cm. Absorption corrections were made, but were very small since the linear absorption coefficient is 24·8 cm.$^{-1}$.

The intensities were measured independently for the many equivalent planes of a given crystallographic form, and were found to be constant within experimental error. A complete set of intensity data was collected for the smaller crystal sphere while all reflections ($HK0$) and ($HK1$) were measured for the larger sphere. The two sets of intensity data were found to be in perfect agreement except for the very strongest reflections for which the larger crystal sphere gave consistently higher values. These differences could be accounted for quantitatively by assuming that the secondary extinction was slightly greater for the smaller sphere.

In order to minimize small errors due to extinction the least-square refinements were based upon the data obtained with the larger crystal sphere except for the reflections (HKL) with $H \geq K \geq L \geq 2$ which had been measured only for the smaller crystal specimen.

At the last refinement stage secondary correction was applied in accordance with the formula

$$I_{\text{corr.}} = I_{\text{obs.}}[1 - gI_{\text{obs.}}]^{-1} \qquad (1)$$

when g is the extinction coefficient. It should be emphasized that this correction was very small. The largest extinction correction was 8·0% (for $|F_{200}|$), the next largest 3·1% and more than 90% of the reflections were not affected.

Comparison of results for the two crystal specimens shows that the observed structure factors per unit cell are accurate to a probable error of 0·5 electron units. All observations were given equal weight in the refinements, and only one reflection, (960), was found to have an intensity too small to be measured.

The f-curves of McWeeny (1951) were used for hydrogen and boron atoms, and that of Berghuis *et al.* (1955) for the oxygen atom.

Determination of the structure

All attempts to find a structure on the basis of space group $Pm3n$ failed, and accordingly the non-centrosymmetrical subgroup $P\bar{4}3n$ was assumed to be correct.

In deducing the structure extensive use was made of the exceptionally large observed structure factor for (800), and of the fact that oxygen–oxygen and boron–boron distances less than 2·2 Å are improbable. With these boundary conditions the special space group positions could be eliminated as possible atomic sites and so could large volumes about symmetry axes and symmetry centers for general positions. This trial and error procedure led without excessive effort to an approximate structure for boron and oxygen atoms agreeing sufficiently well with observations to serve as starting point for a successful least square refinement using the Busing–Levi IBM-704 program.

The first refinement, in which only scale factors and boron and oxygen coordinates were varied and with a fixed overall temperature factor (guessed to be $B = 0{\cdot}90$ Å^2), gave an R-factor of 0·073. The results led to a short $\mathrm{O_{I}}$–$\mathrm{O_{II}}$ distance of 2·49 Å between oxygen atoms bonded to different boron atoms which could only be ascribed to the presence of a hydrogen bond. Accordingly the midpoint of this short oxygen–oxygen connection line was used as initial site for the hydrogen atom in the next refinement.

Table 1. *Results of Refinements*

Variable		Refinement II	Refinement III
K_1*		0·911 ±0·005	0·906 ±0·004
K_2*		0·908 ±0·007	0·903 ±0·007
B			
	x	0·2171 ± 0·0003	0·2172 ± 0·0004
	y	0·0816 ± 0·0004	0·0816 ± 0·0004
	z	0·3092 ± 0·0004	0·3094 ± 0·0004
	B	0·45 ±0·06	
$\mathrm{O_{I}}$			
	x	0·0803 ± 0·0002	0·0804 ± 0·0002
	y	0·1670 ± 0·0002	0·1671 ± 0·0002
	z	0·3004 ± 0·0002	0·3004 ± 0·0002
	B	0·42 ±0·04	
$\mathrm{O_{II}}$			
	x	0·3222 ± 0·0002	0·3223 ± 0·0002
	y	0·1449 ± 0·0002	0·1447 ± 0·0002
	z	0·4261 ± 0·0002	0·4262 ± 0·0002
	B	0·45 ±0·04	
H			
	x	0·937 ±0·007	
	y	0·103 ±0·006	
	z	0·337 ±0·006	
	B	4·8 ±1·9	
R		0·035	0·033

* K_1 is the scale factor for reflections $HK0$ and $HK1$, while K_2 is the scale factor for reflections $H \geq K \geq L \geq 2$.

The second refinement provided for a small extinction correction, the hydrogen atoms were taken into account and individual isotropic temperature factors were used. In the course of this refinement, which gave $R = 0{\cdot}035$, the hydrogen atom moved along the short $\mathrm{O_{I}}$–$\mathrm{O_{II}}$ vector from the initial symmetrical site to a position 1·06 ± 0·06 Å from the $\mathrm{O_{II}}$-atom. The results of this second refinement are shown in column 2 of Table 1.

The possibility of hydrogen resonance

Because of the approximations inherent in the least square method (assumptions of spherical electron distributions and precisely known f-curves) one cannot expect to improve upon the R-factor of 0·035 in further refinements. Hence, the success of additional refinements must be judged on the basis of the physical situation rather than in terms of reduction of the R-factor.

A least square refinement using anisotropic thermal factors was seemingly unsuccessful because the temperature factor of hydrogen became negative (although positive well within the probable error) in directions normal to the $\mathrm{O_{II}}$–H · · · $\mathrm{O_{I}}$ axis. However, the results for boron and oxygen atoms were physically reasonable. The temperature factor for boron remained isotropic within the probable error. For the oxygen atoms a small anisotropy was found with the direction of maximum displacement normal to the three bonds formed by each oxygen atom. Parallel to the $\mathrm{O_{II}}$–H · · · $\mathrm{O_{I}}$ axis the refinement gave a very large

Table 2. *Temperature factors*

Refinement III

$\beta \times 10^3$	B	$\mathrm{O_{I}}$	$\mathrm{O_{II}}$
β_{11}	1·27 ± 0·37	1·33 ± 0·25	0·94 ± 0·25
β_{22}	1·33 ± 0·38	0·94 ± 0·26	1·72 ± 0·26
β_{33}	1·45 ± 0·38	1·48 ± 0·26	1·32 ± 0·23
β_{12}	−0·27 ± 0·31	−0·17 ± 0·22	−0·10 ± 0·22
β_{13}	0·20 ± 0·30	0·08 ± 0·24	−0·05 ± 0·23
β_{23}	−0·06 ± 0·39	0·06 ± 0·23	−0·07 ± 0·20

Table 3. *Root mean square displacements along principal axes*

Refinement III

	Δ_1 (Å)	Δ_2 (Å)	Δ_3 (Å)
B	0·064 ± 0·013	0·073 ± 0·012	0·083 ± 0·010
$\mathrm{O_{I}}$	0·059 ± 0·009	0·074 ± 0·008	0·078 ± 0·007
$\mathrm{O_{II}}$	0·061 ± 0·008	0·073 ± 0·007	0·084 ± 0·006

Table 4. *Orientation of principal axes from refinement* III

Atom	Axis	X	Y	Z
B	1	140 ± 26°	126 ± 39°	75 ± 50°
	2	100 ± 52	55 ± 51	37 ± 49
	3	128 ± 28	55 ± 37	123 ± 47
$\mathrm{O_{I}}$	1	110 ± 22	158 ± 24	82 ± 20
	2	35 ± 69	112 ± 24	116 ± 85
	3	117 ± 78	88 ± 37	153 ± 81
$\mathrm{O_{II}}$	1	169 ± 28	98 ± 16	98 ± 33
	2	99 ± 33	82 ± 25	12 ± 28
	3	84 ± 15	169 ± 22	81 ± 25

Table 5. *Observed and calculated structure factors*

		Refinement III	Refinement II		
HKL	F obs.	KxF calc.	KxF calc.	A	B
110	30.6	30.1	30.4	-33.4	0
200	81.2	83.5	82.8	-90.8	0
210	28.6	29.0	29.3	-32.2	0
211	33.6	34.2	34.7	-11.9	-36.2
220	36.5	35.6	35.3	-38.7	0
310	41.1	41.4	42.1	46.2	0
222	57.6	59.5	59.3	63.6	-14.7
320	10.5	10.4	11.2	-12.3	0
321	30.0	29.6	29.7	23.0	23.2
400	74.2	73.5	73.5	-80.7	0
410	22.3	22.6	22.7	24.9	0
330	71.3	70.8	70.4	-77.2	0
411	22.3	22.0	22.0	4.6	-23.7
420	20.2	19.0	18.9	20.7	0
421	70.9	68.7	69.1	24.3	-71.8
332	42.6	41.9	41.7	-40.9	20.8
422	21.3	19.4	19.7	-0.2	-21.7
430	12.0	10.9	11.0	12.1	0
510	14.8	14.5	14.6	-16.0	0
431	11.6	10.3	10.4	-9.0	7.0
520	9.4	9.1	9.0	-9.9	0
432	7.1	7.0	6.7	3.8	6.4
521	19.1	18.0	18.1	-12.6	-15.3
440	9.2	9.3	9.1	10.0	0
530	36.7	36.2	36.0	39.5	0
433	33.3	32.4	32.3	22.8	-27.2
531	21.2	20.7	20.6	-18.4	-13.1
600	17.6	16.4	15.6	17.1	0
442	9.4	8.7	8.2	-1.9	8.9
610	1.1	0.8	0.7	0.8	0
611	22.9	22.9	23.4	6.1	24.9
532	19.1	18.0	18.1	19.2	-5.1
620	35.4	34.7	34.9	38.2	0
621	17.6	17.6	17.8	-15.5	-11.9
540	15.5	15.0	15.4	16.9	0
541	7.4	6.5	6.4	2.8	-6.4
622	47.6	48.3	48.4	-46.3	26.5
630	13.0	12.2	12.4	-13.7	0
542	39.4	39.9	40.3	-11.7	42.8
631	27.1	26.6	27.0	-19.9	21.9
444	42.7	42.2	42.5	-0.7	46.8
632	7.9	7.5	7.5	0	-8.3
710	1.9	1.6	1.4	1.5	0
550	21.2	20.8	20.8	-22.8	0
543	14.2	13.5	13.5	-14.9	0.4
640	9.1	8.9	8.8	-9.7	0
720	5.5	4.9	4.5	-5.0	0
641	16.2	16.1	15.9	17.3	2.7
721	11.9	12.3	12.4	-1.8	-13.5
633	38.6	39.1	39.1	42.9	-3.4
552	11.3	10.5	10.3	-9.4	6.3
642	2.2	2.4	2.5	-2.0	-1.9
730	2.4	1.2	1.4	-1.5	0
731	30.5	31.1	30.9	26.5	21.2
650	3.7	2.9	3.2	3.5	0
643	9.3	9.6	9.9	-2.9	10.5
732	2.6	2.8	2.8	2.4	-1.9
651	16.1	16.2	16.1	17.7	1.5
800	71.6	73.2	73.0	-80.1	0
810	3.6	3.4	3.4	-3.7	0
740	23.4	24.1	24.0	26.3	0
652	12.6	12.9	12.8	-14.1	0.3
811	13.0	13.0	12.8	13.9	2.5
741	3.8	3.8	3.8	0.9	-4.0
554	25.8	26.3	26.2	12.6	26.0
820	18.8	18.4	18.5	20.3	0
644	34.7	35.9	35.8	0.2	-39.4
821	30.2	30.8	30.7	1.3	33.6
742	27.8	28.0	27.8	-7.5	-29.7
653	26.2	26.1	26.1	-25.8	-12.7
822	21.6	22.7	22.8	1.1	-25.1
660	34.0	35.9	35.6	-39.1	0
830	13.5	14.3	14.4	-15.8	0
831	22.5	22.0	22.2	-16.6	-17.9
750	3.5	4.1	3.8	-4.1	0
743	15.0	15.0	14.9	-0.2	16.4
751	27.9	28.6	28.6	-30.9	5.4
662	36.3	37.5	37.6	38.7	14.9
832	4.3	4.6	4.3	1.5	-4.5
654	16.7	16.4	16.3	13.6	11.8
752	10.8	10.6	10.5	1.1	-11.5
840	16.5	17.0	17.0	18.7	0
841	9.2	9.8	9.7	-10.4	2.5
910	1.6	1.6	1.4	-1.6	0
833	23.2	22.8	23.0	20.7	14.6
753	25.0	24.1	24.2	26.7	1.3
842	6.6	6.8	6.9	-6.3	4.2
920	2.5	2.4	2.2	2.5	0
760	18.2	17.9	18.2	-20.0	0
921	21.6	22.5	22.9	4.6	24.7
761	2.5	2.4	2.4	-2.3	1.3
655	14.2	13.6	13.7	11.2	-10.1
664	6.8	6.5	6.7	3.9	6.2
850	11.9	13.0	13.0	14.3	0
843	20.4	19.2	19.1	-8.1	-19.4
762	4.4	3.7	3.7	2.5	-3.3
930	8.3	8.4	8.2	-9.1	0
851	4.6	4.9	5.1	4.6	-3.1
754	4.7	4.5	4.2	1.3	-4.5
931	9.7	9.2	9.4	-7.8	-6.8
852	9.1	8.6	8.5	3.9	8.6
932	6.4	5.5	5.7	-3.7	5.0
763	9.3	8.6	8.4	-0.4	9.2
844	8.8	7.6	7.9	-2.7	8.3
940	5.9	6.2	6.1	-6.7	0
941	8.9	9.0	9.2	3.5	9.5
853	14.5	12.9	13.0	-11.3	8.7
770	1.0	0.9	1.0	1.0	0
10.0.0	16.3	15.9	15.9	17.5	0
860	5.5	4.9	5.2	-5.7	0
10.1.0	11.8	12.1	12.0	13.2	0
942	5.5	4.6	4.6	-5.1	-0.3
861	9.7	9.7	9.9	10.6	2.2
764	2.3	2.3	2.4	1.0	-2.4
10.1.1	2.6	1.6	1.7	0.7	1.7
772	2.2	1.4	1.2	-0.3	-1.2
10.2.0	6.2	5.8	5.8	-6.4	0
862	11.8	10.8	11.0	-4.3	-11.3
10.2.1	8.7	9.2	9.1	9.8	-2.0
854	11.7	11.1	11.2	-12.3	-1.3
950	5.1	4.8	4.8	5.3	0
943	18.1	17.3	17.4	1.0	-19.1
951	17.5	17.1	16.7	14.2	-11.7
10.2.2	6.5	6.1	5.7	2.2	5.8
666	28.3	28.6	28.9	-31.3	5.8
10.3.0	4.1	3.8	4.4	4.8	0
863	8.1	8.3	8.2	2.0	8.8
10.3.1	17.7	17.2	17.1	-0.5	-18.7

Table 5 (*cont.*)

	Refinement III		Refinement II		
HKL	F obs.	KxF calc.	KxF calc.	A	B
952	9.0	8.3	8.4	0.9	9.2
765	4.6	4.1	4.0	-2.4	3.8
10.3.2	13.6	13.5	13.1	2.6	14.2
870	8.4	8.6	8.6	9.4	0
871	5.4	5.0	5.0	1.9	5.2
855	10.2	9.5	9.5	10.1	-2.8
774	6.0	6.0	6.2	-1.9	-6.5
953	4.9	5.1	5.4	-3.2	5.0
10.4.0	2.2	2.1	2.0	-2.2	0
864	15.0	14.5	14.3	3.7	15.3
10.4.1	14.5	12.9	12.7	6.3	-12.4
960	0	0.1	0.5	0.5	0
872	12.5	11.4	11.4	-1.0	-12.5
10.3.3	3.3	3.1	3.1	-3.1	1.3
961	8.1	8.1	7.9	-5.4	-6.8
10.4.2	7.8	7.8	7.6	0.5	8.4
962	11.0	11.6	11.3	7.5	10.0
11.1.0	1.6	1.5	1.5	1.6	0
954	16.2	16.4	16.6	-1.9	-18.2
873	13.8	14.1	13.8	4.2	-14.6
11.2.0	3.5	3.4	3.6	-4.0	0
10.5.0	8.7	9.4	9.6	-10.5	0
10.4.3	11.7	11.4	11.1	-0.2	12.3
865	4.9	4.8	4.9	-2.5	-4.8
11.2.1	9.0	9.2	9.5	-1.9	-10.3
10.5.1	2.9	2.4	2.3	-0.6	2.5
963	5.2	5.1	5.1	4.9	2.6
880	18.2	18.0	18.0	19.7	0
874	15.8	16.5	16.2	-16.7	-6.5
11.3.0	6.0	5.9	5.6	6.1	0
970	6.6	7.4	7.1	7.8	0

thermal factor for hydrogen, corresponding to a root mean square displacement of 0·37 ± 0·08 Å. The latter result indicates appreciable resonance with the configuration $O_{II} \cdots H\text{–}O_I$.

It is readily shown that (for small values of $\sin\theta/\lambda$) the structure factor contribution of a resonating hydrogen atom is equivalent to that of a single atom at position $\bar{\mathbf{r}} = p\mathbf{r}_1 + (1-p)\mathbf{r}_2$ with a temperature factor

$$B + 8\pi^2 p(1-p)\delta^2 \cos^2 \varphi \, . \qquad (2)$$

$\mathbf{r}_1$ and $\mathbf{r}_2$ are the two equilibrium positions corresponding to the two configurations $O_{II}\text{–}H \cdots O_I$ and $O_{II} \cdots H\text{–}O_I$, while p and $1-p$ are the fractions of time the hydrogen atom spends at $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively. The quantity $\boldsymbol{\delta} = \mathbf{r}_2 - \mathbf{r}_1$, and φ is the angle between $\boldsymbol{\delta}$ and the normal to the reflecting lattice plane. The anisotropic term in the thermal factor due to the resonance has the value $8\pi^2 p(1-p)\delta^2$ parallel to the $O_{II}\text{–}H \cdots O_I$ axis and vanishes at right angles to this direction. For $\delta = 0{\cdot}5$ Å and $p = 0{\cdot}75$ one finds $8\pi^2 p(1-p)\delta^2 = 3{\cdot}8$ Å^2.

A least-square refinement ('refinement III') was made on the assumption of partial resonance, $p = 0{\cdot}75$. For hydrogen a value $B = 3{\cdot}2$ Å^2 was adopted and the coordinates for $\mathbf{r}_1$ and $\mathbf{r}_2$ were so chosen as to give O–H = 1·0 Å. Thus only scale factors and positional and thermal parameters for boron and oxygen atoms were varied. The results of this refinement are given in the tables in the columns headed 'Refinement III'.

The slight lowering of the R-factor from 0·035 to 0·033 has no physical significance. It is probable, however, that there is some resonance with the configuration $O_{II} \cdots H\text{–}O_I$, but the X-ray data provide no conclusive proof.

Description of the structure

Each boron atom is bonded tetrahedrally to four oxygen atoms (two O_I and two O_{II}), and each oxygen atom to two boron atoms, so as to produce a three-dimensional network of BO_4 tetrahedra. The boron–oxygen configuration is thus reminiscent of the structures found for the various forms of silica. However, the bond angles $B\text{–}O_I\text{–}B = 118{\cdot}6 \pm 0{\cdot}1°$ and $B\text{–}O_{II}\text{–}B = 126{\cdot}7 \pm 0{\cdot}1°$ are appreciably smaller than the corresponding Si–O–Si values.

The dimensions of the BO_4 tetrahedron and of the group $O\text{–}H \cdots O$ are:

	(Å)		(Å)
$B\text{–}O_I$	1·436 ± 0·004	$O_I\text{–}O_I'$	2·413 ± 0·003
$\text{–}O_I'$	1·465	$\text{–}O_{II}$	2·431
$\text{–}O_{II}$	1·505	$\text{–}O_{II}'$	2·360
$\text{–}O_{II}'$	1·482	$O_I'\text{–}O_{II}$	2·381
		$\text{–}O_{II}'$	2·421
		$O_{II}\text{–}O_{II}'$	2·412
$H \cdots O_I$	1·43 ± 0·06	$O_I \cdots H\text{–}O_{II}''$	2·487 ± 0·003
$H\text{–}O_{II}''$	1·06		

Fig. 1 shows two pairs of BO_4 tetrahedra of the structure as viewed along the Z-axis to illustrate the

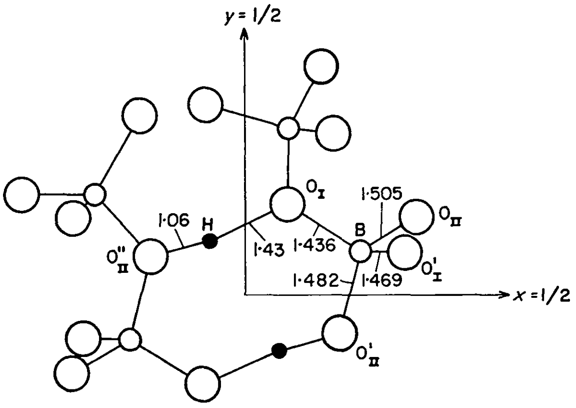

Fig. 1. Small portions of the three-dimensional tetrahedral network and the hydrogen bonds between tetrahedra. The view is along the Z-axis and the z-coordinates for the labelled atoms are: B(0·3092), H(0·337), O_I(0·3004), O_I(0·1670), O_{II}(0·4261), O_{II}'(0·3551), O_{II}''(0·3551). The various bond lengths are shown in Å.

hydrogen binding. It should be kept in mind that there may be appreciable resonance with the configuration O_I–H · · · O_{II} which is not shown in Fig. 1.

The mean value of 1·472 Å for the tetrahedral B–O bond is precisely the same as found in β-HBO_2 (Zachariasen, 1963). Slightly larger tetrahedral bond lengths of 1·477 Å and 1·479 Å have been found in $K[B_5O_6(OH)_4].2\,H_2O$ (Zachariasen & Plettinger, 1963) and in $K_2[B_4O_5(OH)_4].2\,H_2O$ (Marezio, Plettinger & Zachariasen, 1962).

It might have been expected that the two B–O_I bonds would be of equal length; but they do in fact differ by 0·029 Å. This difference (and the similar difference of 0·023 Å in the length of the two B–O_{II} bonds) may be ascribed to interaction between next nearest neighbors.

However, the fact the mean B–O_I bond length of 1·451 Å is much smaller than the mean B–O_{II} bond length of 1·494 Å is a consequence of the hydrogen binding. Since the O_{II} oxygen atom is bonded more strongly to hydrogen, the O_{II}–B bond is correspondingly weakened, while the opposite situation pertains to the O_I atom. Indeed, it is possible to put these considerations on a quantitative basis, as will be demonstrated in a forthcoming paper which discusses results for a number of precisely determined borate structures.

The observed length of 2·487 ± 0·003 Å for the O_{II}–H · · · O_I group is appreciably smaller than corresponding distances in other boric acid structures. In H_3BO_3 (Zachariasen, 1954) the O–H · · · O distance is 2·720 Å and in β-HBO_2 it is 2·681 Å. However, the results for the O–H · · · O group in γ-HBO_2 are identical within experimental error with those obtained from a neutron diffraction study of the ferroelectric form of KH_2PO_4 (Bacon & Pease, 1953, 1955), which gave O–H = 1·05 ± 0·01 Å, O···H = 1·43 ± 0·01 Å and O–H · · · O = 2·486 ± 0·004 Å.

Compared with the α- and β-forms of HBO_2 the γ-form has high density, high refractive index, great hardness and small thermal vibrations. The interrelationship between crystal structure and physical properties for the various modifications of metaboric acid will be discussed in another paper.

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