Acta Cryst. (1954). **7**, 305

The Precise Structure of Orthoboric Acid

By W. H. Zachariasen

Physics Department, University of Chicago, and Argonne National Laboratory, Chicago, Ill., U.S.A.

(*Received* 29 *October* 1953)

The crystal structure of orthoboric acid has been redetermined. The triclinic unit cell, containing four molecules $B(OH)_3$, has dimensions $a_1 = 7{\cdot}039$ Å, $a_2 = 7{\cdot}053$ Å, $a_3 = 6{\cdot}578$ Å, $\alpha_1 = 92{\cdot}58°$, $\alpha_2 = 101{\cdot}17°$, $\alpha_3 = 119{\cdot}83°$.

The 42 parameters in the structure were determined with the aid of precise intensity measurements made with a Geiger-counter spectrometer. The structure is built up of $B(OH)_3$ molecules. These molecules are linked together by hydroxyl bonds, $O\text{–}H \cdots O$, to form endless layers of nearly hexagonal symmetry. The structure can be regarded as a stack of such layers 3·181 Å apart and held together by van der Waals forces.

The bond distances within a $B(OH)_3$ molecule are B–O = 1·361 Å, O–H = 0·88 Å, with a value of 114° for the oxygen bond angle. The $O\text{–}H \cdots O$ distance between molecules is 2·720 Å.

Introduction

The approximate structure of orthoboric acid, $B(OH)_3$, was described nearly twenty years ago (Zachariasen, 1934). The crystals are triclinic with space group symmetry $P\bar{1}$ and four molecules per unit cell. The 24 parameters for the boron and oxygen atoms were determined with the aid of qualitative intensity estimates. The structure was found to contain BO_3-groups with B–O = 1·36 Å arranged in layers parallel (001) with a layer separation of 3·18 Å. A shortest distance of 2·71 Å was found between oxygen atoms of different BO_3-groups within a given layer. Since the number of these short oxygen–oxygen separations was equal to the number of hydrogen atoms it was concluded that these oxygen separations of 2·71 Å corresponded to O–H–O bonds. A value of 120° was found for all bond angles $B\text{–}O \wedge O\text{–}H\text{–}O$, and as a consequence it was assumed that the hydrogen atom was located midway between the two oxygen atoms. Were the bonding between oxygen atoms of the type $O\text{–}H \cdots O$, different values would be expected for the bond angles $B\text{–}O \wedge O\text{–}H \cdots O$ and $B\text{–}O \wedge O \cdots H\text{–}O$. Weighty arguments favoring unsymmetrically placed hydrogen atoms in $B(OH)_3$ were subsequently forwarded by Bernal & Megaw (1935).

Because of the interest of the writer in other boric acids it was decided to carry out a careful structure determination of orthoboric acid, and specifically to try to locate the hydrogen atoms directly from the intensity data.

The experimental procedure

Small, pseudo-hexagonal needles, elongated along the a_3-axis, were used in the investigation. Specimens of this shape are readily obtained from aqueous solution, but nearly all are twinned. Several crystals entirely free of twinning were eventually found. The diameter of the needles used for intensity measurements was 0·006 cm. or less, so that absorption could be completely neglected. The vapor pressure of orthoboric acid is appreciable at room temperature, and small crystals will accordingly vanish by sublimation in the course of a few months if left unprotected in the open air. The crystals used in the investigation were coated with a thin film of grease to reduce the sublimation.

All intensity measurements were made with a modified XRD–3 spectrometer using Cu $K\alpha$ radiation. The modifications of the commercial model of the spectrometer making it suitable for single crystal work are as follows. The commercially-supplied slit systems and sample holder were replaced by pinhole systems of conventional design and by a graduated circle with a goniometer head. The circle is provided with a tangent screw so that the crystal can be finely adjusted about the vertical axis and independently of the setting of the Geiger counter about the same axis. The support of the Geiger counter was changed so as to permit motion also about a horizontal axis with a maximum azimuth angle of 50°. The spectrometer was readjusted so as to give an angle of 10° between the axis of the crystal pinhole system and the target surface.

In the course of the last several years a great mass of experimental data has been taken with this spectrometer under various experimental conditions and for a great number of crystals of various sizes. It has been found that the integrated intensity can be accurately measured with a stationary crystal and a stationary counter, i.e. with a convergent-beam technique, provided the following precautions are taken. In order to attain sufficient uniformity in the convergent beam incident upon the crystal the radiation active in the diffraction must originate in a small central segment of the focal spot. This condition can be met by using a small crystal (linear dimensions of 0·03 cm.

or less) and a large angle (10°) between the X-ray beam and the target surface. The same central segment of the focal spot must clearly be used in order to be sure of the constancy of the incident intensity. Similarly, care must be taken that the path of the diffracted beam within the counter is as nearly as possible the same from one reflection to the next. As a consequence of the last two considerations the intensity was maximized with respect to small variations in the setting of the crystal and of the counter.

The Geiger counter was found to be linear to better than 1% up to counting rates of 800 counts per sec. Calibrated filters of nickel foil were used to reduce the counting rate to the linear range. In the actual experiments with orthoboric acid the measurable integrated intensity range was 10000:1.

The boron and oxygen positions

The old and the new values for the unit-cell dimensions are:

	1934	1953
a_1	7·05±0·04 Å	7·039±0·002 Å
a_2	7·05	7·053
a_3	6·57	6·578
α_1	92·50°	92·58±0·02°
α_2	101·17°	101·17°
α_3	120°	119·83°

Careful intensity measurements were made for all possible planes H_1H_20 and H_1H_21, a total of 315 distinct reflections. The approximate structure being known, the actual parameter determinations were carried out with the aid of a series of Fourier syntheses. In the final synthesis of each type all observable amplitudes were included with correct signs. It is believed that these syntheses give a high degree of precision for the boron and oxygen positions. In the first place the intensities were measured with high precision, and, since extinction was found to be negligible, there is corresponding accuracy in the experimental structure-factor values. Secondly, boric acid crystals are very soft with a high root-mean-square value for the amplitude of thermal vibration, thus minimizing the 'termination-of-series error'. Lastly, the measurable intensity range was unusually large so that errors due to the omission of small Fourier terms at low index values are virtually eliminated.

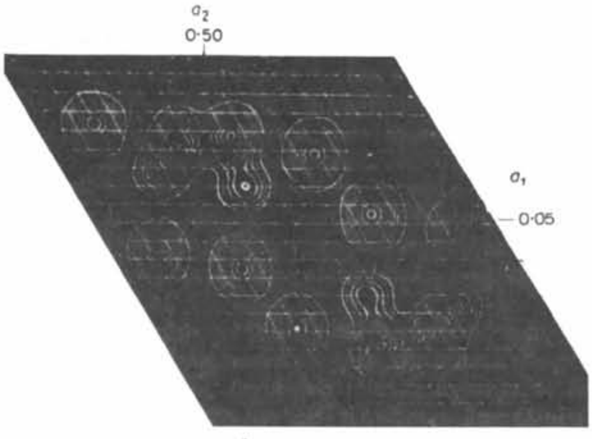

Fig. 1. The synthesis $\int_0^1 \varrho dz$ as photographed on XRAC.

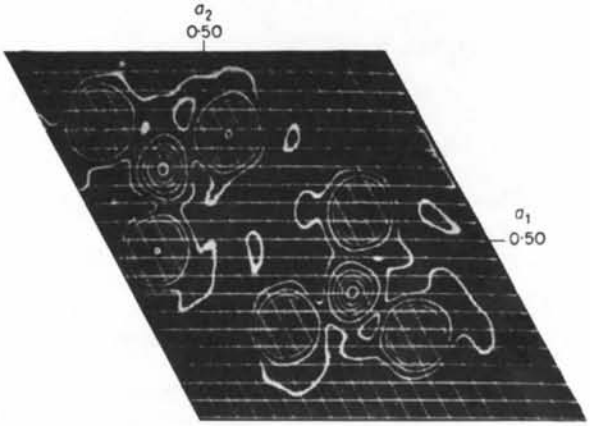

Fig. 2.

The XRAC photograph of the synthesis $\int_0^1 \varrho[1+\sin 2\pi z]dz$. As compared with Fig. 1, the atoms with $z \approx \frac{3}{4}$ have been eliminated.

Preliminary x, y coordinates for boron and oxygen atoms were obtained from the synthesis $\int_0^1 \varrho dz$, the XRAC photograph of which is shown in Fig. 1. Because of superposition, this synthesis was unable to give reliable results for all boron and oxygen atoms. The final x, y coordinates were therefore determined with the aid of the generalized projection

$$\int_0^1 \varrho[1+\sin 2\pi z]\,dz\,,$$

which almost completely eliminates contributions from the atoms at $z \approx \frac{3}{4}$. The XRAC photograph of this synthesis is shown in Fig. 2, while Table 1 contains the final x, y coordinates. The lowest contour line shown in Fig. 2 indicates the presence of the hydrogen atoms to be discussed in the next section.

In the 1934 investigation it was found that the z coordinates for all atoms were $z=\frac{1}{4}$. Precise intensity measurements now being available for a great many pairs of reflections H_1H_21 and $H_1H_2\bar{1}$, it becomes possible to detect small deviations of the z parameters from the ideal value of $\frac{1}{4}$. The generalized synthesis $\int_0^1 \varrho \cos 2\pi z\, dz$ was used for this purpose. The coefficients of the corresponding Fourier series are $F_{H_1H_21}+F_{H_1H_2\bar{1}}$, which are numerically small quantities. However, these coefficients should not vanish, even if all $z=\frac{1}{4}$, owing to the triclinic symmetry.

Simple considerations will show that an atom at $z=\frac{1}{4}$ will give rise to a maximum and a minimum in

Table 1. *Boron and oxygen parameters*

		1934	1953*
B_{I}	x	0·652	0·646
	y	0·430	0·427
	z	0·250	0·258
B_{II}	x	0·319	0·307
	y	0·764	0·760
	z	0·250	0·242
O_{I}	x	0·430	0·424
	y	0·319	0·302
	z	0·250	0·261
O_{II}	x	0·764	0·768
	y	0·319	0·328
	z	0·250	0·250
O_{III}	x	0·764	0·744
	y	0·652	0·650
	z	0·250	0·261
O_{IV}	x	0·541	0·532
	y	0·875	0·885
	z	0·250	0·250
O_{V}	x	0·208	0·214
	y	0·541	0·540
	z	0·250	0·244
O_{VI}	x	0·208	0·180
	y	0·875	0·856
	z	0·250	0·233

* Estimated maximum errors are 0·001 for x and y coordinates, 0·003 for z coordinates.

the function $\int_0^1 \varrho \cos 2\pi z\,dz$, the height of the maximum being equal to the depth of the minimum. Furthermore, if x, y are the true coordinates of the atom in question, the maximum will occur at $x+\Delta_1$, $y+\Delta_2$, the minimum at $x-\Delta_1$, $y-\Delta_2$, where Δ_1 and Δ_2 depend upon the lattice geometry. If the atom is displaced from $z=\frac{1}{4}$ towards lower z values, the maximum increases in height while the minimum decreases in depth. Simultaneously the coordinates of the maximum will approach, and those of the minimum recede from, the true x, y values of the atom.

The XRAC photograph of the synthesis $\int_0^1 \varrho \cos 2\pi z\,dz$ is shown in Fig. 3. A careful analysis of the magnitude and the location of the various maxima and minima led to the z parameters given in Table 1. The improvement in the numerical agreement between observed and calculated values of $F_{H_1H_2 1}+F_{H_1H_2\bar{1}}$ resulting from the small shifts of the z parameters away from $z=\frac{1}{4}$ is illustrated in Table 2.

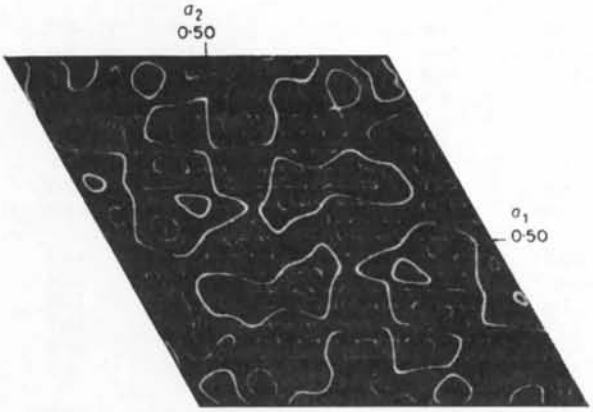

Fig. 3. The synthesis $\int_0^1 \varrho \cos 2\pi z\,dz$. The scale in this figure is ten times that of Fig. 2. The zero contour line appears heavier than the rest. The photograph includes both positive and negative contour lines.

Table 2. *The effect of the z parameters*

	$F_{H_1H_2 1}+F_{H_1H_2\bar{1}}$		
		Calc.	
$H_1H_2H_3$	Obs.	$z=\frac{1}{4}$	z from Table 1
$1\bar{1}1$	−4·2	0·6	−4·5
101	3·5	0·3	3·7
111	4·5	0·5	4·0
$3\bar{3}1$	4·5	0·5	3·5
031	−6·2	−2·0	−5·6

The hydrogen positions

Although Fig. 2 shows the approximate whereabouts of the hydrogen atoms it is difficult to make a reliable determination of the hydrogen positions with the aid of this synthesis owing to the superimposed small contributions from boron and oxygen atoms at $z \approx \frac{3}{4}$. In order to fix the hydrogen positions it seemed unavoidable to use a difference synthesis, and the following one, designed to bring out the hydrogen atoms at $z \approx \frac{1}{4}$, was utilized:

$$\int_0^1 [\varrho-\varrho\,(\mathrm{B+O})][1+\sin 2\pi z]\,dz\,.$$

The evaluation of the coefficients in this series required the introduction of scattering power curves for boron and oxygen atoms for the first time in the investigation.

The f-curves given in the *International Tables* were used, and these were reduced by the factor

Table 3. *Hydrogen parameters*

		1934	1953*
H_{I}	x	0·32	0·347
	y	0·43	0·361
	z	0·25	(0·255)
H_{II}	x	0·65	0·671
	y	0·10	0·172
	z	0·25	(0·250)
H_{III}	x	0·99	0·890
	y	0·76	0·709
	z	0·25	(0·252)
H_{IV}	x	0·65	0·600
	y	0·76	0·817
	z	0·25	(0·254)
H_{V}	x	0·99	0·083
	y	0·43	0·469
	z	0·25	(0·246)
H_{VI}	x	0·32	0·297
	y	0·10	0·006
	z	0·25	(0·243)

* Estimated maximum error is 0·010 for x and y coordinates.

Table 4. *The effect of hydrogen atoms*

	$F_{H_1H_20}$			$F_{H_1H_21}-F_{H_1H_2\bar{1}}$		
		Calc.			Calc.	
H_1H_20	Obs.	Without hydrogen	With hydrogen	Obs.	Without hydrogen	With hydrogen
$2\bar{3}0$	−10·1	−9·1	−10·7	37·1	31·3	36·5
$1\bar{3}0$	−10·4	−11·2	−10·7	55·9	59·6	57·0
$3\bar{2}0$	−1·6	−1·5	−1·5	59·1	65·3	62·3
120	11·1	8·6	10·3	−35·3	−29·9	−34·9
$3\bar{1}0$	11·4	9·1	10·8	33·5	29·6	34·6
210	30·2	32·0	30·5	−18·0	−19·6	−18·8

Table 5. *Observed and calculated structure factors*

	$H_3=-1$		$H_3=0$		$H_3=+1$	
H_1H_20	F_c	$\lvert F_o\rvert$	F_c	$\lvert F_o\rvert$	F_c	$\lvert F_o\rvert$
$1\bar{1}0$	13·1	13·5	−18·8	18·2	−17·6	17·7
$2\bar{2}0$	27·8	27·2	−4·0	4·8	−28·2	26·9
$3\bar{3}0$	11·6	13·2	7·5	7·7	−8·1	8·7
$4\bar{4}0$	−2·9	4·0	−13·7	14·3	3·3	3·8
$5\bar{5}0$	4·7	4·4	−8·0	8·8	−4·3	4·2
$6\bar{6}0$	−3·8	4·4	1·3	2·0	4·3	4·7
$7\bar{7}0$	−3·6	3·4	−1·1	1·1	3·5	3·0
010	−11·7	12·3	−20·8	20·1	13·6	12·4
020	−25·7	23·8	−12·1	13·0	24·5	22·1
030	−16·0	16·7	3·0	2·6	10·4	10·5
040	10·5	11·9	−9·8	10·1	−9·2	9·8
050	2·0	2·6	−8·8	8·6	−1·6	1·9
060	1·3	0	3·3	3·8	−1·3	0
070	3·4	3·2	2·8	2·3	−2·9	2·4
100	4·8	5·1	−23·7	21·1	−1·1	1·7
200	7·8	8·5	−27·7	26·0	−8·3	8·7
300	5·9	6·5	−13·4	14·8	−6·5	6·3
400	−8·0	8·6	12·0	11·7	6·5	6·2
500	−6·1	6·3	5·8	5·7	5·1	4·6
600	2·4	3·2	−2·1	1·7	−0·9	1·1
700	3·3	3·0	−1·8	1·4	−3·1	2·2
$1\bar{2}0$	−7·3	9·0	2·2	2·2	6·5	7·8
$2\bar{4}0$	−1·6	2·0	−4·5	4·8	2·8	3·1
$3\bar{6}0$	16·1	15·4	−16·3	17·0	−16·8	16·3
$4\bar{8}0$	1·7	1·3	0·7	0·7	−1·7	1·3
$2\bar{1}0$	−6·0	7·3	5·2	6·0	4·2	5·2
$4\bar{2}0$	−5·6	5·7	−0·6	0·9	5·9	6·0
$6\bar{3}0$	−11·6	12·7	−19·3	18·2	10·0	10·0
$8\bar{4}0$	0·4	0	−2·2	1·8	−0·1	0
110	4·8	4·5	7·4	8·7	−0·8	0
220	6·7	6·3	4·1	4·0	−4·8	5·8
330	22·9	21·9	5·5	5·3	−19·2	17·5
440	2·1	1·8	0	0	−1·4	1·0
$2\bar{3}0$	−18·2	18·6	−10·7	10·1	18·3	18·5
$1\bar{3}0$	−27·6	27·5	−10·7	10·4	29·4	28·4
$3\bar{2}0$	−33·4	31·7	−1·5	1·6	28·9	27·4
120	18·3	20·5	10·3	11·1	−16·6	14·8
$3\bar{1}0$	−18·3	18·6	10·8	11·4	16·3	14·9
210	9·8	9·8	30·5	30·2	−9·0	8·2
$3\bar{4}0$	6·1	6·3	14·2	14·7	−5·5	5·8
$1\bar{4}0$	9·8	10·8	14·9	15·4	−11·2	12·5
$4\bar{3}0$	13·6	15·2	13·8	13·2	−12·5	13·2
130	−14·4	13·0	0·4	0·8	13·0	13·2
$4\bar{1}0$	13·5	14·5	−7·0	6·7	−10·5	10·5
310	−2·4	2·9	−18·0	17·4	1·6	1·6

$\exp[-B(\sin\theta/\lambda)^2]$ to take account of the heat motion. Anisotropy in the thermal vibration could be neglected since all experimental data referred to reflections for which $H_3 = 0$ or 1. The value of B giving the best fit was found to be $B = 2{\cdot}37\times10^{-16}$ cm.^{2}, which corresponds to a root-mean-square amplitude (at room temperature) of 0·17 Å in the plane of the BO_3-group.

The generalized difference synthesis for the hydrogen atoms is shown in Fig. 4, the three lowest contour lines having been omitted. It should be emphasized that the synthesis shows only the six maxima indicated in Fig. 4. The heights of these maxima range from 7 to 10 contour lines, and there is considerable distortion as regards the shape. The x, y coordinates of the six maxima, presumed to represent hydrogen atoms, are listed in Table 3. It did not prove possible to decide whether or not the z parameters deviated from the value $z = \frac{1}{4}$. The z values given in parenthesis in Table 3 are obtained on the assumption that the hydrogen atoms be as nearly as possible on the connecting lines between oxygen atoms.

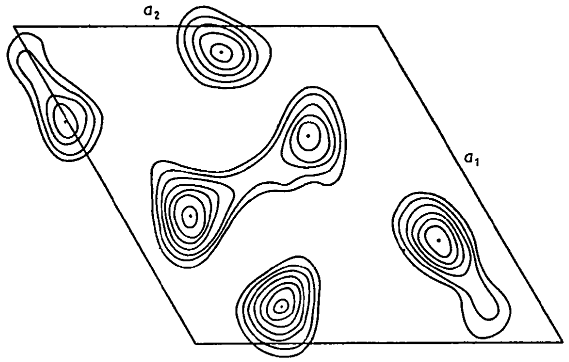

Fig. 4. The generalized difference synthesis $\int_0^1 \varrho[1+\sin 2\pi z]dz$, where ϱ represents the difference between the actual electron density and that due to spherically symmetrical oxygen and boron atoms located at the positions given in Table 1.

Table 6. *Calculated structure factors, F_c, for missing reflections*

H_1H_20	F_c	H_1H_21	F_c	H_1H_21	F_c
$5\bar{4}0$	0·2	111*	−0·8	$6\bar{7}1$	−1·3
410	−0·3	$2\bar{5}1$	0·3	161	0·6
$6\bar{4}0$	−0·1	$1\bar{5}1$	−0·4	$8\bar{4}1$	−0·2
420	−0·4	$5\bar{4}1$	−0·7	$8\bar{3}1$	−0·6
$5\bar{7}0$	0·5	$41\bar{1}$†	−0·3	$2\bar{8}1$	−0·9
$2\bar{7}0$	−0·5	$2\bar{6}1$	0·5	$8\bar{6}1$	−1·1
$7\bar{5}0$	−0·4	$6\bar{4}1$	−0·2	261	0·6
520	0·1	421	0·1	621	−0·3
$6\bar{7}0$	0·6	511	−0·6	$7\bar{8}1$	−0·2
440	0	061	−1·3	$17\bar{1}$	−0·3
$2\bar{8}0$	0·5	$7\bar{4}1$	1·0	$8\bar{1}\bar{1}$	−0·6
$8\bar{6}0$	0·3	$2\bar{7}1$	−0·3		
$7\bar{8}0$	0·3	$7\bar{5}1$	0·2		
$1\bar{8}0$	0·1	521	−0·6		

* $11\bar{1}$ $F_c = 4{\cdot}8$ and $|F_o| = 4{\cdot}6$
† 411 $F_c = -0{\cdot}8$ and $|F_o| = 1{\cdot}3$

The fact that hydrogen atoms did show up in the difference synthesis implies that the numerical agreement between observed and calculated structure amplitudes is improved when the hydrogen atoms are taken into account. This is indeed illustrated in Table 4 for a pseudohexagonal prism and pyramid.

Table 5 shows the degree of agreement for a number of reflections. The R factor is 0·09 for all reflections and 0·07 for those listed in Table 5. Calculated structure factors for the complete set of reflections found to be too weak to be measured are given in Table 6.

Discussion of the structure

The atoms in orthoboric acid crystals are arranged in layers, the structure of one layer being shown in Fig. 5. The constituents of a layer are $B(OH)_3$ molecules which are linked together by hydroxyl bonds O–H ··· O, as was suggested by Bernal & Megaw (1935).

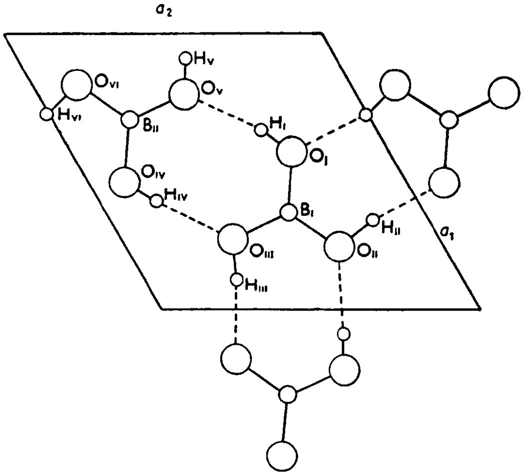

Fig. 5. The structure of one layer of orthoboric acid.

The significant interatomic distances and bond angles are shown in Table 7. The hydrogen atoms are

Table 7. *Interatomic distances and bond angles*

Distances

B_I–O_I	1·365 Å	B_{II}–O_{IV}	1·365 Å
B_I–O_{II}	1·356	B_{II}–O_V	1·353
B_I–O_{III}	1·365	B_{II}–O_{VI}	1·359
O_I–O_{II}	2·351	O_{IV}–O_V	2·339
O_{II}–O_{III}	2·359	O_V–O_{VI}	2·360
O_{III}–O_I	2·366	O_{VI}–O_{IV}	2·362
O_I–H_I	0·83	O_{IV}–H_{IV}	0·83
O_{II}–H_{II}	0·96	O_V–H_V	0·80
O_{III}–H_{III}	0·90	O_{VI}–H_{VI}	0·96
O_I–$H_I \cdots O_V$	2·727	O_{IV}–$H_{IV} \cdots O_{III}$	2·722
O_{II}–$H_{II} \cdots O_{IV}$	2·716	O_V–$H_V \cdots O_{II}$	2·734
O_{III}–$H_{III} \cdots O_{VI}$	2·715	O_{VI}–$H_{VI} \cdots O_I$	2·707

Bond angles B–O ∧ O–H ··· O

O_I	112·9°	O_{IV}	114·2°
O_{II}	116·1	O_V	113·6
O_{III}	113·4	O_{VI}	113·3

situated, within experimental error, on the O ··· O connecting lines between neighboring molecules. The only important differences between the 1934 and 1953 results are in the location of the hydrogen atoms and in the bond angles B–O ∧ O–H ··· O and B–O ∧ O ··· H–O, as the following comparison shows:

	1934	1953 (Mean values)
B–O	1·36 Å	1·361 Å
O–H ··· O	2·71 Å	2·720 Å
O–H	1·36 Å	0·88 Å
O ··· H	1·36 Å	1·84 Å
B–O ∧ O–H ··· O	120°	113·9°
B–O ∧ O ··· H–O	120°	126·1°

The observed value of 0·88 Å is about 0·1 Å smaller than anticipated. This is probably due to the fact that spherically symmetrical oxygen atoms were assumed in the procedure used to deduce the hydrogen positions. Presumably there is an excess of electron density in the oxygen atom near the hydrogen atom, and by the assumed spherical symmetry for oxygen this excess density is inappropriately assigned to hydrogen, resulting in an apparent displacement of the hydrogen towards the oxygen atom.

The layers are not perfectly plane as was concluded in 1934. However, the displacements out of the plane $z = \frac{1}{4}$ are very small, amounting to a maximum value of 0·11 Å for the O_{VI} atom. The idealized layers $z = \frac{1}{4}$ and $\frac{3}{4}$ are 3·181 Å apart, so that only weak bonds exist between layers, in agreement with the observed perfect basal cleavage.

The layers are stacked in such a manner that a number of oxygen atoms are approximately below or above boron and hydrogen atoms of neighboring layers. The shortest B ··· O distances between layers are 3·157 Å ($B_{II} \cdots O_{II}$) and 3·184 Å ($B_{I} \cdots O_{V}$). It appears that these boron–oxygen interactions dominate the hydrogen–oxygen interactions between layers in determining the actual values of the angles α_1 and α_2. And it seems also that the small tilts of the BO_3-groups relative to the plane (001) are mainly due to the interactions between boron and oxygen atoms.

Were all atoms situated exactly at $z = \frac{1}{4}$ without interaction between layers, then perfect trigonal symmetry should prevail in a layer. The small departure from trigonal symmetry actually observed (a_1 and a_2 differing by 0·2%, $\alpha_3 = 119{\cdot}83°$ instead of 120°) is indeed a direct consequence of the small tilts of the BO_3-groups relative to the plane $z = \frac{1}{4}$ caused by weak interaction between layers.

The help given by Miss Anne Plettinger in making some of the intensity measurements is gratefully acknowledged. Most of the Fourier syntheses used in the investigation were carried out with the aid of XRAC during three separate visits to Pennsylvania State College. Prof. Raymond Pepinsky is sincerely thanked for his hospitality and generosity in making XRAC available to the writer. The writer is also indebted to the XRAC staff members for the help they have given.

References

Bernal, J. D. & Megaw, H. D. (1935). *Proc. Roy. Soc.* A, **151**, 384.
Zachariasen, W. H. (1934). *Z. Kristallogr.* **88**, 150.

Acta Cryst. (1954). **7**, 310

On the Completion and Extension of the Table of Atomic Scattering Factors Published by Viervoll & Ögrim

By M. M. Qurashi*

Department of Physics, The Pennsylvania State College, State College, Pa., U.S.A.

(*Received* 2 *April* 1953 *and in revised form* 23 *October* 1953)

The table of atomic scattering factors (based on the Hartree self-consistent field) published by Viervoll & Ögrim has a gap between calcium ($Z = 20$) and chromium ($Z = 24$). This gap has been bridged by calculating the screening parameter for the (3*d*) electron in $Ca^{+}(3d)$. This calculation has been done by a new method, which has possibilities for use with heavier atoms. The atomic scattering factors for scandium to vanadium are tabulated as functions of $s = 4\pi(\sin\theta)/\lambda$.

Viervoll & Ögrim (1949) have published a revised table of atomic scattering factors, up to atomic number 29 (copper), based on recent calculations of the Hartree self-consistent field for a number of atoms. The metals scandium, titanium and vanadium, however, are omitted from this table because of the uncertain extrapolation of the screening parameters for the (3*d*) electrons. In working on the structures of the mineral vanadates (Barnes & Qurashi, 1952; Qurashi

---

* On leave from the Department of Scientific and Industrial Research, Government of Pakistan, Karachi.