# The Crystal Lattice of Boric Acid, $\mathrm{BO}_{3} \mathrm{H}_{3}{ }^{1}$ ). 

By
W. H. Zachariasen in Chicago.
(With 1 figure.)

## 1. Introduction.

So far we do not know the crystal lattice for any of the oxygenic acids. The role which the hydrogen atoms play in these compounds is therefore entirely unknown or subject to mere speculations. In order to solve this problem a crystal structure investigation of boric acid was undertaken.

The hydrogen atoms, it is true, have only a negligible influence on the amplitude of the scattered radiation, and hence their positions in the lattice cannot be determined directly from the observed intensities of reflections. By applying our knowledge of the interionic distances it should, however, be possible to locate the hydrogen atoms with a fair certainty. This method was used with success in finding the hydrogen positions in sodium bicarbonate ${ }^{2}$ ).

Before attempting to locate the hydrogen atoms in this manner, it is imperative to determine with accuracy the coordinates of all the other atoms in the lattice.

Crystals of boric acid are triclinic pinacoidal. The crystallographic elements are given by Groth ${ }^{3}$ ) as:

$$
a: b: c=1.7329: 1: 0.9228 \quad \alpha=92^{\circ} 30^{\prime} \quad \beta=104^{\circ} 25^{\prime} \quad \gamma=89^{\circ} 49^{\prime}
$$

In this paper we will use another orientation of the crystallographic axes, namely the one that corresponds to the true unit cell of the crystal lattice. The new $b$ and $c$ axes coincide with those of Groth, while the new $a$ axis has zone indices $\frac{1}{2}[1 \overline{1} 0]$ referred to the old set. Hence the transformation formulae for the Miller indices are ( $h k l$ new indices,

[^0]$h^{\prime} k^{\prime} l^{\prime}$ old indices $): h=\frac{1}{2}\left(h^{\prime}-k^{\prime}\right) k=k^{\prime} \quad l=l^{\prime}$. The new elements become:
$a: b: c=0.9990: 1: 0.9228 \quad a=92^{\circ} 30^{\prime} \quad \beta=101^{\circ} 10^{\prime} \quad \gamma=149^{\circ} 51^{\prime}$.
The crystals are pseudo hexagonal, the $c$-axis being the pseudo hexagonal axis. The imitation of a higher symmetry appears also in the optical properties. The acute bisectrix is exactly normal to the $c$-face, the optical axial angle being close to $180^{\circ}$. The obtuse bisectrix nearly coincides with the $b$-axis. For $N a$-light the refractive indices are $^{1}$ ): $\alpha=1.340 \beta=1.456 \gamma=1.459$.

The cleavage which boric acid crystals exhibit parallel to the $c$-face is highly perfect. Like graphite the crystals are very soft and easily deformed.

## 2. Unit Cell and Space Group.

The crystals used in the investigation were obtained by recrystallizations from aqueous solutions. Two distinctly different types of crystals were prepared, namely thin plates parallel to the $c$-face or needles parallel to the $c$-axis. The latter type of crystals was obtained when the growth took place from the surface downwards in the solution.

The Laue method and the oscillating crystal method were employed. For the latter MoKa radiation was used. The wave length of the $\alpha_{1} \alpha_{2}$ doublet was taken to be $0.7095 \AA$. During each exposure the crystal was oscillated through a range of $15^{\circ}$. A complete set of 18 overlapping photographs were taken with the $c$-axis as rotation axis, and in addition a large number of photographs around the two other crystallographic axes and around other prominent directions. The photographs were indexed by means of J. D. Bernals ${ }^{2}$ ) neat graphical method.

The Laue photographs served merely as a check on the unit cell, while all intensity considerations were based upon observations from the oscillation photographs. These observations are entirely reliable in this case, since the absorption can be neglected (very low absorption coeffecient and small crystals). The crystals are very soft, indicating a large temperature effect. Hence the scattering powers decrease very rapidly with increasing value of $\sin \theta / \lambda$ and the intensities of reflection decrease accordingly.

The orientation of the unit cell corresponds to the axial system introduced previously. (The coordinate system used by Groth does

[^1]not correspond to an unreducible cell.) The dimensions of the unit cell are:
\[

$$
\begin{gathered}
a=7.04 \pm .04 \AA \quad b=7.04 \pm .04 \AA \quad c=6.56 \pm .04 \AA \\
\alpha=92^{\circ} 30^{\prime} \quad \beta=101^{\circ} 10^{\prime} \quad \gamma=120^{\circ} .
\end{gathered}
$$
\]

With the accuracy of our methods it was impossible to find any difference in the lengths of the $a$ and $b$ axes, nor did our data indicate that the angle $\gamma$ was different from $120^{\circ}$. The lengths and orientation of the $a$ and $b$ axes consequently correspond to a hexagonal crystal.

There are four molecules of $\mathrm{H}_{3} \mathrm{BO}_{3}$ in the unit cell. The calculated density is 1.48 , while the observed values lie in the range 1.46-1.52.

We have no reason to doubt that the crystals belong to the pinacoidal class, so that we will consider $P \overline{1}\left(C_{i}^{1}\right)$ to be the correct space group. The only elements of symmetry are inversion centers, so that the atoms will occur in pairs with coordinates $\pm(x y z)$ unless they are lying in the symmetry centers. If the latter positions are vacant, there are altogether 42 degrees of freedom in the lattice. Of the 42 parameters 6 are required to fix the boron positions, 18 are required to fix the oxygen positions and the remaining 18 parameters refer to the hydrogen positions. Since the contribution of the hydrogen atoms to the structure amplitude safely can be neglected, we have 24 parameters to deal with when considering the intensities of reflections.

## 3. Determination of the Boron and Oxygen Positions.

The observed intensities are given in table I and II.
Table I. Reflections from the $c$-face.

| $00 l$ | 001 | 002 | 003 | 004 | 005 | 006 | 007 | 008 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | ---: |
| $\sin \theta / \lambda$ | .079 | .158 | .237 | .316 | .394 | .473 | .552 | .631 |
| Int. obs. | nil | vs | nil | s | nil | m | nil | w |
| $F$ calc. | 0 | 92 | 0 | 54 | 0 | 34 | 0 | 27 |

Table II. Observed Intensities from Oscillation Photographs with $c$-Axis as Rotation Axis.

| $h k \overline{3}$ | $h k 2$ | $h k i$ | $h k 0$ | $h k 1$ | $h k 2$ | $h k 3$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| nil | $s+$ | VW | $100 \mathrm{~s}+$ | nil | w | nil |
| w- | s- | $\mathrm{m}+$ | $1 \overline{1} 0 \mathrm{~s}$ | m | m | w |
| w- | s- | $m+$ | 010 s | m | m | w- |
| vw | w- | vw | 110 w | vvw | vW | nil |
| vw | vvw | vw + | $2 \overline{10} \mathrm{vw}$ | vvw | vVW |  |
|  | nil | w | T20 nil | w- | nil | vw |

The Crystal Lattice of Boric Acid, $\mathrm{BO}_{3} \mathrm{H}_{3}$.
Table II (continuation).


The reflections from the $c$-face show interesting features. The odd order reflections are all absent and the intensities of the even order reflections show a "normal decline", the intensities being exceptionally high throughout the series. Another striking regularity is that reflections $h k 0, h k 2, h k \overline{2}, h k 4, h k \overline{4}$ and so on (with $h$ and $k$ constant) appear with the same intensity when allowance is made for the decrease of the scattering powers with increasing $\sin \theta / \lambda$. The same applies to the series $h k 1, h k \overline{1}, h k 3, h k \overline{3} \ldots$

These observations show definitely that the atoms are evenly distributed between two layers parallel to the $c$-face, the $z$-coordinates for the layers being either 0 and $\frac{1}{2}$, or $\frac{1}{4}$ and $\frac{3}{4}$. The vertical distance between consecutive atomic layers is $3.18 \AA$.

In other crystals boron has been found to be surrounded either by four or by three oxygen atoms, the latter being the usual configuration in borates proper. Only the coordination number three is compatible with the known distribution of the atoms in the $z$-direction. Having thus found that the structure contains $\mathrm{BO}_{3}$-groups arranged parallel to the $c$-face, it becomes logical to make use of our knowledge of the dimensions of these groups, as we know from experience that groups of this kind will not materially alter its shape or dimensions from one crystals to another. In hambergite ${ }^{1}$ ) the $B-O$ distance was found to be $1.36 \AA$ and in calcium metaborate ${ }^{2}$ ) $1.35 \AA$. The $B O_{3}$ group is like the nitrate and carbonate group coplanar.

By making use of the known structure of the ortho-borate group the problem of determining the crystal lattice was greatly simplified. Still further simplifications were obtained from considerations of interatomic distances. It is safe to assume that the smallest oxygen-oxygen distance must be the one in the $B O_{3}$-groups, so that the distance between oxygen atoms of different $B O_{3}$-groups can be put greater than $2.35 \AA$.

With these assumptions it was a comparatively easy task to determine the coordinates of the boron and oxygen atoms. As mentioned previously we had two possibilities to consider for the $z$-parameters: 1. all equal to 0 and $\frac{1}{2}, 2$. all equal to $\frac{1}{4}$. The first possibility was readily disproved.

The final parameter values are given in table III. The proof that these coordinates are the correct ones is the good agreement between observed intensities and calculated amplitudes in table IV. In view of the fact that reflections $h k 0, h k 2, h k \overline{2} \ldots$ and reflections $h k 1, h k \overline{1}$, $h k 3 \ldots$ have identical amplitudes (when allowance is made for the variation

1) W. H. Zachariasen, Z. Krist. 76, 289. 1931.
2) W. H. Zachariasen and G. E. Ziegler, Z. Krist. 83, 354. 1932.

Table III. Final Parameter Values (given in angular measure).

|  | $2 \pi x$ | $2 \pi y$ | $2 \pi z$ |
| :--- | ---: | ---: | :---: |
| $B_{\mathrm{I}}$ | $235^{\circ}$ | $155^{\circ}$ | $90^{\circ}$ |
| $B_{\mathrm{II}}$ | 145 | 275 | 90 |
| $O_{\mathrm{I}}$ | 155 | 415 | 90 |
| $O_{\mathrm{II}}$ | 275 | 145 | 90 |
| $O_{\mathrm{III}}$ | 275 | 235 | 90 |
| $O_{\mathrm{IV}}$ | 75 | 195 | 90 |
| $O_{\mathrm{V}}$ | 75 | 315 | 90 |
| $O_{\mathrm{VI}}$ | 195 | 315 | 90 |
| $H_{\mathrm{I}}$ | 145 | 155 | 90 |
| $H_{\mathrm{II}}$ | 115 | 35 | 90 |
| $H_{\mathrm{III}}$ | 355 | 155 | 90 |
| $H_{\mathrm{IV}}$ | 235 | 35 | 90 |
| $H_{\mathrm{V}}$ | 355 | 275 | 90 |
| $H_{\mathrm{VI}}$ | 235 | 275 | 90 |

Table IV. Calculated Amplitudes and Observed Intensities (observations from Oscillation Photographs around $c$-axis).

| $h k 0$ | $2 \sin \theta$ | F | $I$ | $h k 1$ | $2 \sin \theta$ | $F$ | $I$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $1 \overline{10}$ | .117 | 21 | s | 1T1 | . 154 | 10 | m + |
| 010 | . 118 | 23 | s | 014 | . 148 | 15 | $\mathrm{m}+$ |
| 100 | . 120 | 27 | $\mathrm{s}+$ | $10 \overline{1}$ | . 142 | 3 | vw |
| 120 | . 202 | 3 | nil | $1 \overline{2} 1$ | . 226 | 12 | w |
| 210 | . 205 | 9 | vw | $2 \overline{1} \overline{1}$ | . 214 | 8 | vw + |
| 110 | . 207 | 11 | w | 111 | . 211 | 6 | vw |
| $2 \overline{2} 0$ | . 234 | 6 | vw | $2 \overline{2} \overline{1}$ | . 250 | 33 | $s$ |
| 020 | . 236 | 12 | w+ | 027 | . 252 | 32 | s |
| 200 | . 240 | 35 | s | $20 \overline{1}$ | . 252 | 6 | w- |
| $2 \overline{3} 0$ | . 307 | 14 | W | $2 \overline{3} \overline{1}$ | . 327 | 30 | S |
| 130 | . 309 | 11 | w | $1 \overline{3} 1$ | . 318 | 30 | s |
| $3 \overline{2} 0$ | . 316 | 3 | vvw | $3 \overline{2} \overline{1}$ | . 313 | 32 | s |
| 3 10 | . 316 | 21 | w | 311 | . 310 | 25 | m- |
| 120 | . 315 | 14 | w | 121 | . 311 | 30 | m - |
| 210 | . 317 | 30 | s | 217 | . 309 | 14 | w+ |
| $3 \overline{3} 0$ | . 351 | 11 | w- | $3 \overline{3} \overline{1}$ | . 358 | 18 | w + |
| 030 | . 354 | 6 | nil | 03 I | . 353 | 21 | m - |
| 300 | . 360 | 21 | w+ | $30 \overline{1}$ | . 349 | 6 | vw |
| $2 \overline{4} 0$ | . 403 | 7 | vvw | $2 \overline{4} 1$ | . 413 | 4 | nil |
| $4 \overline{2} 0$ | . 410 | 0 | nil | $4 \overline{2} \overline{1}$ | . 404 | 8 | nil |
| 220 | . 414 | 4 | tr | $22 \overline{1}$ | . 403 | 7 | vrw |
| $3 \overline{4} 0$ | .419 | 19 | w | $3 \overline{1}$ | . 431 | 9 | vw- |
| $1 \overline{4} 0$ | . 422 | 18 | w + | 141 | . 424 | 13 | w- |
| $4 \overline{3} 0$ | . 423 | 13 | w | $4 \overline{3} \overline{1}$ | . 422 | 18 | w |
| 130 | . 429 | 4 | vw - | 131 | . 420 | 22 | m - |

Table IV (continuation).

| $h k 0$ | $2 \sin \theta$ | $F$ | $I$ | $h k 1$ | $2 \sin \theta$ | $F$ | $I$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $4 \overline{10}$ | . 431 | 14 | vw | $4 \overline{11}$ | .419 | 18 | w+ |
| 310 | . 433 | 23 | m- | 311 | . 419 | 7 | w |
| $4 \overline{4} 0$ | . 468 | 21 | w | $4 \overline{4} 1$ | . 470 | 8 | vw - |
| 040 | . 472 | 16 | vw + | 041 | . 466 | 14 | w- |
| 400 | . 480 | 21 | w | 401 | . 465 | 8 | vw + |
| 350 | . 507 | 11 | w | 351 | . 517 | 2 | nil |
| 250 | . 508 | 11 | w- | 251 | . 512 | 1 | nil |
| 530 | . 514 | 5 | tr | $5 \overline{3} 1$ | . 507 | 9 | vvw |
| $5 \overline{2} 0$ | . 518 | 1 | nil | $5 \overline{2} 1$ | . 506 | 11 | vw + |
| 230 | . 520 | 1 | nil | $23 \overline{1}$ | . 507 | 11 | w |
| 320 | . 523 | 6 | tr | $32 \overline{1}$ | . 503 | 9 | vVW |
| $4 \overline{5} 0$ | . 533 | 7 | w- | $4 \overline{5} \overline{1}$ | . 540 | 2 | nil |
| $15 \overline{5}$ | . 537 | 7 | nil | 151 | . 534 | 0 | nil |
| 540 | . 537 | 7 | nil | $5 \overline{4} 1$ | . 538 | 2 | nil |
| 140 | . 544 | 5 | vw - | $14 \overline{1}$ | . 529 | 5 | vw |
| $5 \overline{10}$ | . 548 | 3 | nil | $5 \overline{11}$ | . 533 | 6 | vw |
| 410 | . 551 | 7 | nil | 411 | . 527 | 2 | vw- |
| $5 \overline{5} 0$ | . 585 | 15 | vw | $5 \overline{5} \overline{1}$ | . 584 | 6 | tr |
| 050 | . 590 | 15 | vw | 051 | . 581 | 2 | nil |
| 500 | . 600 | 14 | vw | $50 \overline{1}$ | . 582 | 7 | vw - |
| 360 | . 606 | 28 | w | $3{ }^{\mathbf{6}} 1$ | . 610 | 28 | w |
| $6 \overline{3} 0$ | . 615 | 28 | w | $6 \overline{3} \overline{1}$ | . 604 | 28 | w |
| 330 | . 621 | 0 | tr | $33 \overline{1}$ | . 605 | 38 | m |

of the scattering powers with $\sin \theta / \lambda$ ), the calculated structure aplitudes are given only for reflections $h k 0$ and $h k 1$. The minor discrepancies which occur in table IV can, I believe, almost universally be attributed to errors in the visual estimation of the intensities, and possibly also to our somewhat unsatisfactory information concerning the scattering powers. The $f$-curves which were used in the calculations, given in table $V$, refer to free atoms at rest. The temperature effect is very great (boric acid being a soft crystal) and it will be noticed from table IV that the observed intensities "die off" much more rapidly than is indicated by the numerical values of the calculated amplitudes.

Table V. $f$-Curves ${ }^{1}$ ).

| $\sin \theta / \lambda$ | 0 | .1 | .2 | .3 | .4 | .5 |
| :--- | :--- | ---: | ---: | ---: | ---: | ---: |
| $B$ | 5 | 3.6 | 2.5 | 1.9 | 1.7 | 1.5 |
| $O^{-1}$ | 9 | 7.9 | 5.9 | 4.1 | 3.9 | 2.2 |

[^2]
## 4. Determination of the Hydrogen Positions.

As we expected we found good agreement between observed and calculated intensities by neglecting the hydrogen atoms altogether. Thus it becomes impossible to locate the hydrogen atoms by means of intensity considerations, so that we must find other ways of determining the whereabouts of these atoms.

In fig. 1 is given the atomic arrangement in one of the layers of which the crystal is built up. The atomic arrangement in each individual layer is the same, but the layers are displaced with respect to each other in all three directions. The translation along the $z$-axis is $\frac{1}{2}$, so that the distance between consecutive layers is $3.18 \AA$.


Fig. 1 shows the atomic arrangement in one layer. The three dimensional crystal is a pile of such layers. The vertical distance between individual layers is $3.18 \AA$. The adjacent layers are displaced with respect to each other in such a manner that the oxygen atoms of one layer lie almost directly above or below boron and hydrogen atoms of the two neighbouring layers. The atomic arrangement within in each layer is, as nearly as we can tell, perfectly hexagonal. Small filled circles represent boron atoms, large open circles oxygen atoms and small open circles hydrogen atoms.

Considering fig. 1 we notice that some of the oxygen atoms belonging to different $\mathrm{BO}_{3}$-groups are separated by comparatively small distances, namely $2.71 \AA$. Oxygen atoms which are only $2.71 \AA$ apart will repel each other strongly, both due to the ordinary coulomb forces and to the partial overlapping of the electron clouds. These repulsive forces must be balanced by attractive forces. One might explain it by saying that there is co-valent binding between the oxygen atoms. Such
an explanation is, however, impossible. If co-valent bond existed between the oxygen atoms, the distance should be of the order of $1.3-1.5 \AA^{1}$ ). The only likely explanation of the small oxygen to oxygen distances is that the oxygen atoms are linked together by the hydrogen atoms. This interpretation is confirmed by the fact that the number of oxygen to oxygen distances of $2.71 \AA$ is exactly equal to the number of hydrogen atoms which we have to our disposal. By placing the hydrogen atoms in the positions indicated in fig. 1 the $H-O$ distance becomes $1.355 \AA$. The coordinates of the hydrogen atoms are given in table III.

## 5. Discussion of the Structure.

We cannot, of course, prove that the hydrogen positions are correct. We used purely circumstancial evidence; but I think it must be admitted that this evidence is strong. Our conclusions are also supported by the results obtained for acid salts (see p. 159).

The structure exhibits some interesting features. We learnt that all the atoms are evenly distributed between layers parallel to the $c$-face $3.18 \AA$ apart. Because of the large distance separating the layers, only very weak bonds can operate between them, a fact, which directly explains the observed perfect cleavage. Indeed, the boric acid comes very close of being a two dimensional crystal. The atomic arrangement in the twodimensional lattices of which the crystal is built up is, as nearly as we are able to tell, perfectly hexagonal, not only with respect to lattice dimensions, but also with respect to symmetry. Due to the way in which the individual layers are piled on top of each other triclinic symmetry will result for the crystal as a whole, although the hexagonal character appears in a series of properties.

From the peculiar nature of the crystal, as a pile of twodimensional layers, follows that the crystal growth will take place much more rapidly in the layer than normal to it. Hence it is to be expected that the crystals should occur in the shape of thin plates parallel to the $c$-face. This type is, indeed, the common one. However, needleshaped crystals parallel to the $c$-axis were also prepared by the writer. (Groth also mentions this shape.) This anomalous type was obtained if crystallization took place from the surface downwards in the solution. It may be explained in the following manner: When the layers are being formed in the surface of the solution, the expansion of the layers will be checked by the

1) W. H. Zachariasen and R. C. L. Mooney, Z. Krist. in press. The oxygen to oxygen distance in the persulphate group was found to be $1.46 \AA$.
surface tension, forcing the continued growth to take place normal to the layers, thus producing in the end needles.

Since the $B O_{3}$-groups as well as the $O-H-O$ groups are parallel to the $c$-face, it follows that the crystals must exhibit strong negative birefringence. Because of the approximation to hexagonal symmetry, the crystals are furthermore nearly uniaxial. An attempt was made to calculate the refractive indices from the atomic arrangement using the method developed by W. L. Bragg. The results were in qualitative agreement with observations. However, satisfactory agreement can only be obtained, if we give the polarizability of oxygen markedly different values for different directions of the electric vector.

As regards the type of binding between the layers, the following fact may be of importance: The layers are piled together in such a manner that the oxygen atoms of one layer lie almost directly above or below boron and hydrogen atoms of the neighbouring layers. This is made possilbe by the striking feature that the $B-O$ distance is exactly equal to the $H-O$ distance. The distance between the layers is too great for the binding to be of the ordinary ionic or valence type. It is likely that the bonds between layers rather are of the van der Waals type. Indeed, one may think of the formation of the threedimensional boric acid crystal as being essentially an "adsorption" phaenomenon.

It is of interest to compare boric acid with acid oxygen salts. Only for $\mathrm{KH}_{2} \mathrm{PO}_{4}{ }^{1}$ ) and $\mathrm{NaHCO}{ }_{3}{ }^{2}$ ) do we know the crystal structure with any degree of accuracy. In both compounds the hydrogen atoms were found to lie half-way between two oxygen atoms belonging to two different radicals. Thus collinear groups $O-H-O$ were formed, completely analogous to the hydrofluoric ion $(F H F)^{-}$in the acid fluorides. The $\mathrm{O}-\mathrm{O}$ distance in the $\mathrm{O}-\mathrm{H}-\mathrm{O}$ group was found to be $2.54 \AA$ in $\mathrm{KH}_{2} \mathrm{PO}_{4}$ and $2.55 \AA$ in $\mathrm{NaHCO}_{3}$.

In boric acid the hydrogen atoms are arranged according to the same principles as in the known acid salts. Again collinear $\mathrm{O}-\mathrm{H}-\mathrm{O}$ groups are formed and these groups link the $B O_{3}$-radicals together. The $O-O$ distance is somewhat greater, namely $2.71 \AA$. This is not surprising, however, since each oxygen atom is linked to two hydrogen atoms. There will thus be quite a strong repulsion between the hydrogen atoms, which will tend to increase the interatomic distances within the group.

On the basis of our results it seems that the presence of these $O-H-O$ groups is a characteristic property of oxygenic acids in the solid state and of acid oxygenic salts.

[^3]As far as we know no acid nitrates or perchlorates exist. This can be understood on the basis of Paulings principle of balanced valence. Let us consider the general case of a radical $\left(X O_{n}\right)^{-m}$ and find out under which conditions an acid salt can be formed without serious violation of Paulings principle. In the first place we should remark that it is not necessary for our considerations to go into the question of the nature of the binding within the radical. For example in the $\left(\mathrm{SO}_{4}\right)^{-2}$ radical we can assume purely ionic binding by writing $\left(S^{+6} O_{4}^{-2}\right)^{-2}$, or we can assume electron pair binding by writing $\left(S^{+2} O_{4}^{-1}\right)^{-2}$; the conclusions with respect to the point in question are the same for the two cases. We will have to assume, however, that the binding between hydrogen and oxygen is ionic. in character.

In a crystal lattice of an acid salt certain oxygen atoms will be linked up to the central atom $X$ of the radical, to one hydrogen atom and in addition to one or more of the cations. For simplicity let us consider the binding inside the radical to be purely ionic, with a numerical charge of $+z$ on the central ion $X$. Oxygen will then have a charge -2 and hydrogen +1 . The total sum of the bond strengths ending upon such an oxygen atom thus is: $z / n+\frac{1}{2}+k$, where $\frac{1}{2}$ is the contribution from hydrogen (since the coordination number is 2 ) and $k$ the contribution from the metal ions. If the electrostatic principle were to be exactly fulfilled the above sum should equal the numerical charge on oxygen. However, deviations are frequently observed. Empirical results show rather that we should write: $z / n+\frac{1}{2}+k=2.00 \pm 0.25$, or $1.25-k$ $<z / n<1.75-k$. The value of $k$ will, of course, vary from compound to compound, depending upon stoechiometric ratios and coordination number for the metal ions. For $n$ equal to 4 we find that $z<7-4 k$, showing that the central cation certainly must carry a charge numerically less than 7. Thus acid perchlorates may be expected to be unstable. If $n$ is three we get $z<5.25-3 k$. For reasonable values of $k$ the charge of the central ion is brought well below 5 , so that acid nitrates also should be expected to be unstable.

Similar considerations can be made also for other types of radicals, and are, of course, closely related to the strength of the corresponding acids.

## Summary.

Crystals of boric acid are triclinic-holohedral. The unit cell have dimensions $a=7.04 \AA, b=7.04 \AA, c=6.56 \AA$ with angles $\alpha=92^{\circ} 30^{\prime}$, $\beta=101^{\circ} 10^{\prime}, \gamma=120^{\circ}$. There are four molecules $H_{3} B O_{3}$ within the
unit cell. The boron and oxygen positions are characterized by 24 degrees of freedom. The values of these 24 parameters were determined (see table III) from the intensities observed in oscillation photographs. The good agreement between observed and calculated amplitudes proves the correctness of the boron and oxygen positions. The location of the hydrogen atoms require 18 further parameters. These parameter values were found from considerations of interatomic distances.

The structure can conveniently be described as a pile of twodimensional lattices, each having hexagonal symmetry. The layers are $3.18 \AA$ apart and are held together by very weak bonds, thus explaining directly the perfect cleavage and the small rigidity. Each layer is built up of $\mathrm{BO}_{3}$-groups which are held together by the hydrogen atoms. The $B-O$ distance is $1.36 \AA$. Each hydrogen atom is linked to two oxygen atoms forming collinear groups ( $O-H-O$ ) similar to the hydro-fluoric ion. The $O-O$ distance in these groups is $2.71 \AA$.

The presence of the $O-H-O$ groups is a characteristic property of crystalline oxygenic acids and acid salts.

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[^0]:    1) This paper was read before the American Physical Society at the Chicago meeting June $19^{\text {th }}$ 1933. An abstract appeared in Physic. Rev. 44, 327. 1933.
    2) W. H. Zachariasen, J. chem. Physics 1, 634. 1933.
    3) P. Groth, Ch. Kryst., Vol. 1.
[^1]:    1) Internat. Crit. Tables Vol. I, New York 1926.
    2) J. D. Bernal, Pr. Roy. Soc. London (A) 113, 117. 1926.
[^2]:    1) R. W. James and G. W. Brindley, Z. Krist. 78, 470. 1931.
    2) L. Pauling and J. Sherman, ibid. 81, 1. 1932.
[^3]:    4) J. West, Z. Krist. 74, 306. 1930 2) W. H. Zachariasen,.l. c.
