

Note added in proof. — The writer regrets having overlooked a paper by Chandrasekhar (1960), in which it is correctly stated (equation 9) that the proper procedure for handling extinction is to take the mean integrated reflection for parallel and perpendicular components. Thus equation (9) gives the correct formula for the symmetrical Bragg case.

References

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The Structure and Birefringence of Hambergite, $\text{Be}_2\text{BO}_3 \cdot \text{OH}$

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$\text{Be}_2\text{BO}_3(\text{OH})$ is orthorhombic with four molecules in a cell of dimensions $a = 9.755 \text{ \AA}$, $b = 12.201 \text{ \AA}$, $c = 4.426 \text{ \AA}$. The space group is $Pbca$ with all atoms in general positions.

The structure has been redetermined with high precision ($R = 0.04$). Bond lengths are:

$$\text{Be-O} = 1.633 \text{ \AA}, \text{B-O} = 1.367 \text{ \AA}, \text{H-O} = 0.93 \text{ \AA}, \text{H} \cdots \text{O} = 2.04 \text{ \AA}.$$

Refractive indices calculated from the structure agree well with measured values.

Introduction

The approximate crystal structure of the mineral hambergite, $\text{Be}_2\text{BO}_3(\text{OH})$, was reported thirty years ago (Zachariasen, 1931). The original intensity data were crude. As a consequence the results as to bond lengths were quite inaccurate, and the position of the hydrogen atom was assumed rather than deduced from experiment.

It seemed desirable to make a precise determination of the hambergite structure using modern techniques to measure intensities. In the first place it was of interest to obtain accurate values for the Be-O and B-O bond lengths. Second, infrared studies had indicated a bond angle for hydrogen considerably smaller than the 180° usually found in the $\text{O-H} \cdots \text{O}$ bond. Third, an accurate knowledge of the structure could be used to calculate the birefringence of the crystal in a situation where the anisotropic components were not all parallel. The results of the refinement of the structure are presented in the following, together with results of a calculation of the refractive indices of the crystal from the refined structure.

The essential features of the 1931 structure determination have been confirmed; but there is considerable difference in detail.

The refinement of the structure

New values for the cell dimensions are

$$a = 9.755 \pm 0.001, \quad b = 12.201 \pm 0.001, \\ c = 4.426 \pm 0.001 \text{ \AA}.$$

The cell contains four molecules, the space group is $Pbca$, and all atoms are in general positions.

The intensities were measured with an incident beam of unpolarized $\text{Cu K}\alpha$ X-rays, a proportional counter, and a crystal (selected from the original Madagascar material) shaped into a perfect sphere of radius $r = 0.0314 \text{ cm}$, corresponding $\mu r = 0.69$. All reflections $HK0$, $HK1$, $H0L$, $H1L$, $H2L$, $0KL$, $1KL$ were measured.

It was quickly found there was considerable secondary extinction in the specimen, in spite of surface grinding and thermal shock treatment in liquid nitrogen. In the early refinement stages only the weak reflections were therefore used. Since one of the objects of the study was the direct location of the hydrogen atom, it became essential to make corrections for secondary extinction in subsequent refinements. It was then found that the commonly used correction formula was in error (Zachariasen, 1963), and the revised equation was used in the ultimate least-square refinement.

The Busing-Levi IBM-704 program was used with the f curves (for neutral atoms) given in the *International Tables for X-Ray Crystallography*. The initial atomic coordinates were those of the 1931 paper with the hydrogen atom placed midway between two O_{IV} atoms. An isotropic temperature factor, with $B = 2.0 \text{ \AA}^2$, was assumed for the hydrogen atom. In the last refinements all (24) position parameters, 42 anisotropic thermal parameters (for all but the hydrogen atoms) and 4 scale factors were varied simultaneously. Only the final refinement included extinction correction in accordance with the true

theoretical formula, and it gave marked improvement in precision. The results presented in the following are those of the ultimate refinement which was based on 437 reflections and gave a conventional R index of 0.041 (including the 'zeros'). Tables of experimental and calculated F values will be omitted; but they are available on request.

Results

Since the general features of the structure are the same as reported in 1931 a detailed description can be omitted.

Table 1. *Position parameters*
($\times 10^4$)

	x	y	z	σ	σ	σ
Be _I	0029	4	1882	3	2600	10
Be _{II}	2375	3	0676	3	2775	8
B	1059	3	1072	2	7719	8
O _I	0377	2	1875	1	6199	4
O _{II}	1013	2	1029	1	0815	4
O _{III}	1867	2	0346	1	6181	4
O _{IV}	3399	2	1729	1	2956	5
H	3117	38	2170	33	4554	99

Table 2. *Thermal parameters β_{ij}*
($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Be _I	18 ± 2	13 ± 2	104 ± 17	1 ± 2	-4 ± 7	15 ± 7
Be _{II}	18 ± 3	14 ± 2	80 ± 15	2 ± 2	-8 ± 8	-1 ± 7
B	13 ± 2	11 ± 1	118 ± 15	-3 ± 2	-16 ± 7	-5 ± 6
O _I	21 ± 2	8 ± 1	48 ± 9	3 ± 1	-9 ± 5	-7 ± 3
O _{II}	17 ± 2	11 ± 1	72 ± 10	4 ± 1	-4 ± 4	6 ± 4
O _{III}	19 ± 2	11 ± 1	51 ± 9	5 ± 1	12 ± 4	-2 ± 3
O _{IV}	14 ± 1	14 ± 1	107 ± 10	-3 ± 1	3 ± 4	-13 ± 4

Table 3. *Bond lengths (in Å)*

	O _I	O _{II}	O _{III}	O _{IV}
Be _I	1.629	1.621		1.619
	1.673			
Be _{II}		1.644	1.612	1.629
			1.638	
B	1.362	1.372	1.367	
H				0.93
				2.04

The values of the positional and thermal parameters are shown in Tables 1 and 2, while Table 3 gives the bond lengths. The standard errors for the interatomic distances are as follows: 0.002 Å for O-O, 0.004 Å for Be-O and B-O, 0.04 Å for H-O.

The oxygen triangle about boron is nearly perfect (edges 2.365, 2.366 and 2.371 Å), and so is the oxygen tetrahedron about the Be_{II} atom (edges ranging from 2.651 to 2.671 Å). There is some distortion of the Be_IO₄ tetrahedron with edges varying from 2.601 to 2.743 Å.

The mean bond lengths are Be-O = 1.633 Å and

B-O = 1.367 Å, the mean tetrahedral edge 2.665 Å and the mean triangular edge 2.367 Å.

The hydrogen atom is bonded to an O_{IV} atom (as suggested in 1931) to form an OH group, but there is also a weak bond H...O_{IV} so it is justifiable to refer to a group O_{IV}-H...O_{IV}. The separation O_{IV}-O_{IV} = 2.905 ± 0.002 Å, H-O_{IV} = 0.93 ± 0.04 Å, H...O_{IV} = 2.04 ± 0.04 Å, with the hydrogen displaced about 0.3 Å from the O_{IV}-O_{IV} connection line. This displacement can be attributed to H-Be repulsion. The actual distances are H-Be_I = 2.12 ± 0.04 Å, H-Be_{II} = 2.11 ± 0.04 Å. Were the hydrogen atom situated on the oxygen-oxygen connection line, the H-Be_I distance would be significantly reduced and the H-Be_{II} separation correspondingly increased.

Vergnoux & Ginouvès (1955) have studied a crystal of hambergite in the near infrared, and reached the conclusion from their data that the hydrogen atom was considerably displaced off the O_{IV}-O_{IV} connection line. They determined the direction of the O_{IV}-H bond in the structure and gave -0.31, 0.29 and 0.9 Å for the components of the bond along the X, Y, Z axes (assuming 1.00 Å for the length). These values should be compared with the components -0.27, 0.54, 0.70 Å found in the present paper. The X-ray work does, indeed, confirm that the hydrogen atom is displaced in the manner deduced from the infrared data.

Table 4. *Thermal data*

	i	Δ_i (Å)	α	β	γ
Be _I	1	0.076 ± 0.014	0.29	-0.68	0.68
	2	0.095 ± 0.007	0.96	0.24	-0.16
	3	0.120 ± 0.009	-0.07	0.69	0.72
Be _{II}	1	0.080 ± 0.013	0.68	-0.21	0.69
	2	0.095 ± 0.011	-0.48	0.59	0.64
	3	0.108 ± 0.008	0.54	0.79	-0.31
B	1	0.061 ± 0.013	0.81	0.41	0.42
	2	0.098 ± 0.007	-0.41	0.91	-0.07
	3	0.116 ± 0.008	-0.42	-0.10	0.91
O _I	1	0.059 ± 0.009	0.10	0.50	0.86
	2	0.079 ± 0.007	-0.48	0.78	-0.39
	3	0.109 ± 0.004	0.87	0.34	-0.33
O _{II}	1	0.067 ± 0.008	0.56	-0.62	0.56
	2	0.091 ± 0.006	-0.50	0.29	0.82
	3	0.102 ± 0.005	0.67	0.73	0.14
O _{III}	1	0.056 ± 0.010	-0.50	0.34	0.78
	2	0.087 ± 0.006	-0.36	0.74	-0.56
	3	0.111 ± 0.005	0.78	0.57	0.24
O _{IV}	1	0.078 ± 0.006	0.82	0.50	0.28
	2	0.088 ± 0.007	-0.53	0.48	0.69
	3	0.121 ± 0.006	-0.23	0.72	-0.67

Table 4 gives the data of Table 2 in terms of the root mean square amplitudes Δ_i along principal axes and the direction cosines of the principal axes in the XYZ system of the crystal. The thermal amplitudes are small, as was to be expected from the great hardness of the crystal, and the anisotropy is moderate.

The normal of the BO_3 triangle has direction cosines $\alpha_1=0.793$, $\alpha_2=0.605$, $\alpha_3=0.070$, and it is seen from Table 4 that the three oxygen atoms have their largest amplitude nearly parallel to this direction.

The refractive indices

It may be assumed, as a very good approximation, that the oxygen atoms are entirely responsible for the optical refractivity in the visible region. Let δ be the polarizability of an isolated oxygen atom. Since the atomic positions of the oxygens are known to great precision, it should be possible to calculate the refractive indices for the substance if δ is known or treated as an adjustable constant.

The oxygen atoms, O_I , O_{II} , O_{III} form a highly anisotropic configuration about boron while O_{IV} is in nearly isotropic surroundings. Accordingly it will be assumed that O_{IV} has the normal polarizability δ for any direction of the electric vector. The polarizability per stoichiometric molecule is $\delta(1+3q)$, where q is an anisotropy factor for O_I , O_{II} , O_{III} which depends upon the direction of the electric field. In order to calculate q , dipole-dipole interaction will be considered only between oxygens of the same BO_3 group. The manner in which such calculations can be performed has been described by Bragg (1924), and by this writer (Zachariasen, 1933).

When the electric vector is normal to the BO_3 group, one has (see the references)

$$q_{\perp} \simeq 1/(1+2\delta/r^3)$$

where r is the O-O distance, and for the electric vector lying in the plane of the triangle

$$q_{\parallel} \simeq (1+5\delta/3r^3)/(1+\delta/r^3).$$

A value $\delta=1.350 \times 10^{-24}$ will be assumed. Setting $r=2.367 \text{ \AA}$, the result is $q_{\perp}=0.831$ and $q_{\parallel}=1.062$. The corresponding values for the polarizability per stoichiometric molecule are thus: $\Sigma\delta_{\perp}=4.713 \times 10^{-24}$ for normal and $\Sigma\delta_{\parallel}=5.652 \times 10^{-24}$ for parallel electric vector.

The direction of the normal to the BO_3 group in the structure is $u=0.793i+0.605j+0.070k$. Let α , β , γ denote the values of the refractive index when the electric vector is along the X , Y , or Z direction of the crystal. The values of the polarizability per molecule in these directions are

$$\begin{aligned}\delta_{\alpha} &= 0.371 \Sigma\delta_{\parallel} + 0.629 \Sigma\delta_{\perp} \\ \delta_{\beta} &= 0.634 \Sigma\delta_{\parallel} + 0.366 \Sigma\delta_{\perp} \\ \delta_{\gamma} &= 0.995 \Sigma\delta_{\parallel} + 0.005 \Sigma\delta_{\perp},\end{aligned}$$

and the refractive index α is given by

$$\alpha^2 = 1 + 4\pi N \delta_{\alpha} / (1 - 4\pi N \delta_{\alpha} / 3)$$

with analogous expressions for β and γ , where N is the number of stoichiometric molecules per cm^3 .

The calculated and observed values (for Na light) are given below:

	calculated	observed
α	1.557	1.560
β	1.590	1.591
γ	1.638	1.631

The value of the single parameter, $\delta=1.350 \times 10^{-24}$ was chosen so as to give the best fit, but otherwise only the structural information was used. The agreement is remarkable in view of the simplicity of the theoretical model.

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