8. The Crystal Structure of Bixbyite and the *C*-Modification of the Sesquioxides.

By

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(With six figures.)

1. Introduction.

It was discovered in 1925 by Goldschmidt[1]) that an extensive series of sesquioxides form cubic crystals with the unit of structure containing 16 M_2O_3, the value of a varying between 9.3 Å and 10.9 Å. An atomic arrangement based on the space group T^5 was assigned this *C*-modification of the sesquioxides by Zachariasen[2]), who studied crystals of Sc_2O_3, Mn_2O_3, Y_2O_3, In_2O_3, Tl_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and the mineral bixbyite, $(Fe, Mn)_2O_3$. Zachariasen's procedure was the following. Using data from powder and Laue photographs of Tl_2O_3, and neglecting the contribution of the oxygen atoms to the reflections, he decided that the space group is T^5, with the 32 Tl in 8b with parameter $t = 0.25$, in 12c with parameter $u = 0.021$, and in 12c with parameter $v = 0.542$. These parameter values were assumed to hold for all members of the series. The consideration of intensities of reflection of Sc_2O_3 then was found to indicate the 48 O to be in two groups of 24 in the general position of T^5, with parameters $x_1 \sim \frac{1}{8}$, $y_1 \sim \frac{1}{8}$, $z_1 \sim \frac{3}{8}$ and $x_2 \sim \frac{1}{8}$, $y_2 \sim \frac{3}{8}$, $z_2 \sim \frac{3}{8}$. The same structure was also assigned bixbyite, with 16 $(Mn, Fe)_2O_3$ in a unit 9.35 ± 0.02 Å on edge.

On beginning the investigation of the tetragonal pseudo-cubic mineral braunite, $3\,Mn_2O_3 . MnSiO_3$, we found the unit of structure to be closely related to that of bixbyite, and, indeed, to have dimensions nearly the same as those for two superimposed bixbyite cubes. This led us to

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1) V. M. Goldschmidt, »Geochem. Vert.-Ges. d. El.« IV, V, Videnskapsselsk. Skr., 5, 7, Oslo. 1925. 2) W. Zachariasen, Z. Krist. **67**, 455. 1928; »Untersuchungen über die Kristallstruktur von Sesquioxyden und Verbindungen ABO_3«, Videnskapsselsk. Skr. **4**, Oslo. 1928.

make a study of **Zachariasen**'s structure, leading to the observation that not only are the interatomic distances reported abnormally small, but also the structure does not fall in line with the set of principles found to hold for coordinated structures in general[1]. It was further noted that **Zachariasen**'s atomic arrangement, with the symmetry of space group T^5, approximates very closely an arrangement with the symmetry of T_h^7 (of which T^5 is a sub-group), and it is difficult to find a physical explanation of this distortion from a more symmetrical structure. This led to the reinvestigation of this mineral and the determination of a new and satisfactory structure for the *C*-modification of the sesquioxides.

2. The Unit of Structure and Space-group Symmetry of Bixbyite.

Bixbyite, found only in Utah, about 35 miles southwest of Simpson, is described by **Penfield** and **Foote**[2] as *forming shiny black cubic crystals* with a trace of octahedral cleavage. The composition assigned it by them was $Fe^{++}Mn^{+4}O_3$, with a little isomorphous replacement of Fe^{++} by Mg^{++} and Mn^{++} and of Mn^{+4} by Ti^{+4}. It was shown by **Zachariasen** that the X-ray data exclude this formulation, and indicate instead that the mineral is a solid solution of Mn_2O_3 and Fe_2O_3. We shall reach a similar conclusion.

Table I.

Spectral Data from (100) of Bixbyite
(with rock salt comparison).

hkl	Line	*d/n*	Estimated Intensity	S^2/10,000
200	$MoK\alpha_1$	$\frac{1}{2} \times 9.40$ Å	0.05	0.26
100	α_1	$\frac{1}{4} \times 9.38$	7	21.16
400	α_2	$\frac{1}{4} \times 9.37$		
600	α_1	$\frac{1}{6} \times 9.38$	0.2	0.61
600	α_2	$\frac{1}{6} \times 9.36$		
800	α_1	$\frac{1}{8} \times 9.36$	5	20.0
800	α_2	$\frac{1}{8} \times 9.34$		
10.0.0	α_1	$\frac{1}{10} \times 9.38$	0.1	0.23
10.0.0	α_2	$\frac{1}{10} \times 9.34$		
12.0.0	α_1	$\frac{1}{12} \times 9.36$	0.4	1.80
14.0.0	α_1	$\frac{1}{14} \times 9.37$	0.3	0.71
16.0.0	—	—	0.1	0.71

Average: $a = 9.365 \pm 0.020$ Å.

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[1] **Linus Pauling**, J. Am. chem. Soc, **51**, 1010. 1929.

[2] **S. L. Penfield** and **H. W. Foote**, Z. Krist. **28**, 592. 1897.

Data from oscillation photographs of bixbyite show a to be a multiple of 4.68 Å (Table I). The Polanyi layer-line relation applied to photographs with [100] as rotation axis showed that this multiple must be 2, giving a unit with

$$a = 9.365 \pm 0.020\ \text{Å}.$$

This unit sufficed to account for the occurrence of all spots observed on several Laue photographs taken with a tube operated at a peak voltage of 54 kv. (the incident beam making small angles with [100] or [110]), and may be accepted as the true unit.

Table II.
Laue Data for Bixbyite.
Incident beam nearly normal to (100).

{hkl}	d_{hkl} Å	Estimated Intensity. $n\lambda =$				S Calculated	$S^2/10,000$
		0.25—0.29 Å	0.30—0.34 Å	0.35—0.39 Å	0.40—0.45 Å		
611	1.51				10.0	209	4.37
451	1.44				10.0	172	2.96
415					10.0	157	2.46
631	1.38			7.0	7.0	218	4.75
613				7.0	10.0	—233	5.43
271	1.27		0.4	1.0		119	1.42
217			2.5	3.0		—154	2.37
651	1.18	0.1	0.4			139	1.93
615		0.2	0.4			142	2.02
417	1.15	0.1	0.1			—84	0.71
471			0.8			107	1.14
811	1.15	1.0	1.6			180	3.24
275	1.06				0.0	18	0.03
257					0.1	25	0.06
219	1.01				0.0	11	0.01
291					0.2	30	0.09
293	0.96			0.1	0.1	48	0.18
239				0.1	0.2	43	0.18
277	.93			0.3	0.4	—103	1.06
837	.85				0.6	—102	1.04
873					0.6	—107	1.14
10.5.3	.81			0.1	0.05	—93	0.86
10.3.5					0.1	93	0.86
4.11.3	.77			0.1	0.1	—63	0.40
4.3.11				0.1	0.1	—68	0.46

The value 4.945 for the density of bixbyite reported by **Penfield** and **Foote** leads to $16(Mn, Fe)_2O_3$ in the unit.

It was observed that the only planes giving odd-order reflections (see Table II) were those with $h+k+l$ even, indicating strongly that the structure is based on the body-centered cubic lattice Γ_c''. Moreover, a **Laue** photograph taken with the incident beam normal to (100) showed only two symmetry planes and a two-fold axis, requiring that the point-group symmetry of the crystal be that of T or T_h. The only space groups compatible with these conditions are T^3, T^5, T_h^5, and T_h^7. Of these T_h^7 requires that planes $(0kl)$ with k and l odd give no odd-order reflections, while T^3, T^5, and T_h^5 allow such reflections to occur. On our photographs no such reflections were found, although a number of planes of this type were in positions favorable to reflection (Table III). This makes it highly probable that T_h^7 is the correct space group, for it would be very difficult to account for the absence of these reflections with an atomic arrangement derived from T^3, T^5, or T_h^5 which at the same time did not come indistinguishably close to an arrangement derivable from T_h^7. In view of these considerations we have assumed T_h^7 to be the correct space group.

Table III.

Data for Prism Forms from Bixbyite.

A. Forms not reflecting on **Laue** photographs:

$\{hkl\}$	$n\lambda$	
{071}	0.35,	0.39 Å
{701}	0.34,	0.40
{11.0.3}	0.40,	0.45
{0.11.3}	0.41,	0.44
{13.0.3}	0.30,	0.33
{0.13.3}	0.31,	0.32

B. Forms not reflecting on oscillation photographs:

{031}, {013}, {033}, {051}, {015}, {053}, {035}, {055},
{071}, {017}, {073}, {037}, {075}, {057}, {091}, {019},
{093}, {039}, {095}, {059}.

This choice of space group is further substantiated by **Zachariasen**'s data for the other substances as well as bixbyite. His reproduced **Laue** photographs of Tl_2O_3 and of bixbyite show no spots due to {071}, {017}, {091}, {019}, {0.11.1} or {0.1.11}, although planes of these forms were in positions favorable to reflection, while the powder data show that {031}, {013}, {073}, and {037} gave no reflections for any of the sesquioxides studied. **Zachariasen**'s rejection of T_h^7 arose from his assumption that the oxygen contribution to the intensities was negligible, and his consequent inability to account for the observed inequalities in intensity of pairs of forms such as {271} and {217} with the metal atoms in positions provided by T_h^7. But actually the oxygen contribution is by no means negligible. For example, the structure which we find gives for the metal contributions to the structure factor for {271} and {217} the values $+ 66.2$ and $- 66.2$, which are changed by the oxygen contribution to $+ 119.6$ and $- 154.2$, respectively. For Tl_2O_3 the effect of the oxygen would be only about one-fourth as great, which is, however, still sufficient to account for the observed inequalities[1].

3. The Arrangement of the Metal Atoms.

The equivalent positions provided by T_h^7 are:

$8i$: $0\,0\,0;\ \frac{1}{2}\,\frac{1}{2}\,0;\ \frac{1}{2}\,0\,\frac{1}{2};\ 0\,\frac{1}{2}\,\frac{1}{2};$
$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2};\ 0\,0\,\frac{1}{2};\ 0\,\frac{1}{2}\,0;\ \frac{1}{2}\,0\,0.$
$8e$: $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4};\ \frac{1}{4}\,\frac{3}{4}\,\frac{3}{4};\ \frac{3}{4}\,\frac{1}{4}\,\frac{3}{4};\ \frac{3}{4}\,\frac{3}{4}\,\frac{1}{4};$
$\frac{3}{4}\,\frac{3}{4}\,\frac{3}{4};\ \frac{3}{4}\,\frac{1}{4}\,\frac{1}{4};\ \frac{1}{4}\,\frac{3}{4}\,\frac{1}{4};\ \frac{1}{4}\,\frac{1}{4}\,\frac{3}{4}.$
$16e$: $u\,u\,u;\ u, \bar{u}, \frac{1}{2} - u;\ \frac{1}{2} - u, u, \bar{u};\ \bar{u}, \frac{1}{2} - u, u;$
$\bar{u}\,\bar{u}\,\bar{u};\ \bar{u}, u, u + \frac{1}{2};\ u + \frac{1}{2}, \bar{u}, u;\ u, u + \frac{1}{2}, \bar{u};$
$u + \frac{1}{2}, u + \frac{1}{2}, u + \frac{1}{2};\ u + \frac{1}{2}, \frac{1}{2} - u, \bar{u};\ \bar{u}, u + \frac{1}{2}, \frac{1}{2} - u;\ \frac{1}{2} - u, \bar{u}, u + \frac{1}{2};$
$\frac{1}{2} - u, \frac{1}{2} - u, \frac{1}{2} - u;\ \frac{1}{2} - u, u + \frac{1}{2}, u;\ u, \frac{1}{2} - u, u + \frac{1}{2};\ u + \frac{1}{2}, u, \frac{1}{2} - u.$
$24e$: $u\,0\,\frac{1}{4};\ \bar{u}\,\frac{1}{2}\,\frac{1}{4};\ \frac{1}{2} - u, 0, \frac{3}{4};\ u + \frac{1}{2}, \frac{1}{2}, \frac{3}{4};$
$\frac{1}{4}\,u\,0;\ \frac{1}{2}\,\bar{u}\,\frac{1}{2};\ \frac{3}{4}, \frac{1}{2} - u, 0;\ \frac{3}{4}, u + \frac{1}{2}, \frac{1}{2};$
$0\,\frac{1}{4}\,u;\ \frac{1}{2}\,\frac{1}{4}\,\bar{u};\ 0, \frac{3}{4}, \frac{1}{2} - u;\ \frac{1}{2}, \frac{3}{4}, u + \frac{1}{2};$
$\bar{u}\,0\,\frac{3}{4};\ u\,\frac{1}{2}\,\frac{3}{4};\ u + \frac{1}{2}, 0, \frac{1}{4};\ \frac{1}{2} - u, \frac{1}{2}, \frac{1}{4};$
$\frac{3}{4}\,\bar{u}\,0;\ \frac{3}{4}\,u\,\frac{1}{2};\ \frac{1}{4}, u + \frac{1}{2}, 0;\ \frac{1}{4}, \frac{1}{2} - u, \frac{1}{2};$
$0\,\frac{3}{4}\,\bar{u};\ \frac{1}{2}\,\frac{3}{4}\,u;\ 0, \frac{1}{4}, u + \frac{1}{2};\ \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - u.$
48: $x\,y\,z;\ x, \bar{y}, \frac{1}{2} - z;\ \frac{1}{2} - x, y, \bar{z};\ \bar{x}, \frac{1}{2} - y, z;$
$z\,x\,y;\ \frac{1}{2} - z, x, \bar{y};\ \bar{z}, \frac{1}{2} - x, y;\ z, \bar{x}, \frac{1}{2} - y;$
$y\,z\,x;\ \bar{y}, \frac{1}{2} - z, x;\ y, \bar{z}, \frac{1}{2} - x;\ \frac{1}{2} - y, z, \bar{x};$
$\bar{x}\,\bar{y}\,\bar{z};\ \bar{x}, y, z + \frac{1}{2};\ x + \frac{1}{2}, \bar{y}, z;\ x, y + \frac{1}{2}, \bar{z};$
$\bar{z}\,\bar{x}\,\bar{y};\ z + \frac{1}{2}, \bar{x}, y;\ z, x + \frac{1}{2}, \bar{y};\ z, x, y + \frac{1}{2};$
$\bar{y}\,\bar{z}\,\bar{x};\ y, z + \frac{1}{2}, \bar{x};\ \bar{y}, z, x + \frac{1}{2};\ y + \frac{1}{2}, \bar{z}, x;$
$x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2};\ x + \frac{1}{2}, \frac{1}{2} - y, z;\ \bar{x}, y + \frac{1}{2}, \frac{1}{2} - z;\ \frac{1}{2} - x, \bar{y}, z + \frac{1}{2};$
$z + \frac{1}{2}, x + \frac{1}{2}, y + \frac{1}{2};\ z, x + \frac{1}{2}, \frac{1}{2} - y;\ \frac{1}{2} - z, \bar{x}, y + \frac{1}{2};\ z + \frac{1}{2}, \frac{1}{2} - x, \bar{y};$
$y + \frac{1}{2}, z + \frac{1}{2}, x + \frac{1}{2};\ \frac{1}{2} - y, z, x + \frac{1}{2};\ y + \frac{1}{2}, \frac{1}{2} - x, \bar{x};\ \bar{y}, z + \frac{1}{2}, \frac{1}{2} - x;$
$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z;\ \frac{1}{2} - x, y + \frac{1}{2}, z;\ x, \frac{1}{2} - y, z + \frac{1}{2};\ x + \frac{1}{2}, y, \frac{1}{2} - z;$
$\frac{1}{2} - z, \frac{1}{2} - x, \frac{1}{2} - y;\ z, \frac{1}{2} - x, y + \frac{1}{2};\ z + \frac{1}{2}, x, \frac{1}{2} - y;\ \frac{1}{2} - z, x + \frac{1}{2}, y;$
$\frac{1}{2} - y, \frac{1}{2} - z, \frac{1}{2} - x;\ y + \frac{1}{2}, z, \frac{1}{2} - x;\ \frac{1}{2} - y, z + \frac{1}{2}, x;\ y, \frac{1}{2} - z, x + \frac{1}{2}.$

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[1] Dr. Zachariasen has kindly informed us that he now agrees with our choice of the space group T_h^7.

Of these, all but the general position may be occupied by the metal atoms. The 32 metal atoms may have any one of the following arrangements:

A: Formula, $FeMnO_3$:

1a. $16\,Fe$ in $16e$, $16\,Mn$ in $16e$.
2a. $16\,Fe$ in $16e$, $8\,Mn$ in $8i$, $8\,Mn$ in $8e$.
2b. $16\,Mn$ in $16e$, $8\,Fe$ in $8i$, $8\,Fe$ in $8e$.

B: Formula, $(Mn, Fe)_2O_3$:

1b. $16(Mn, Fe)$ in $16e$, $16(Mn, Fe)$ in $16e$.
2c. $16(Mn, Fe)$ in $16e$, $8(Mn, Fe)$ in $8i$, $8(Mn, Fe)$ in $8e$.
3. $24(Mn, Fe)$ in $24e$, $8(Mn, Fe)$ in $8i$, or
$24(Mn, Fe)$ in $24e$, $8(Mn, Fe)$ in $8e$.

The reflecting powers of Mn and Fe are nearly the same, and may be taken equal without serious error. This reduces the number of distinct structures to three; namely, 1 *ab*, 2 *abc*, and 3, of which 1 *ab* depends on two parameters and the others on one. It is possible to decide among them in the following way. Let us assume that the contribution of oxygen atoms to the intensity of reflection in various orders from (100) is small compared with the maximum possible contribution of the metal atoms; that is, with $32\,\overline{M}$. The metal atom structure factor for structure 1 for $(h00)$ is

$$S_{h00} = 16\,\overline{M}\,(\cos 2\pi h u_1 + \cos 2\pi h u_2).$$

Now (200) gave a very weak reflection, so that S_{200} must be small. This is true only for $u_1 + u_2 \cong \frac{1}{4}$, for which

$$S_{h00} \cong 0 \text{ for } h = 2, 6, 10,$$
$$S_{h00} \cong 32\,\overline{M} \cos 2\pi h u_1 \text{ for } h = 4, 8, 12.$$

Now the gradual decline in intensity for $h = 4, 8, 12$ (Table I) requires that $u_1 = \frac{1}{8}$, and hence $u_2 = \frac{1}{8}$. This puts the two sets of metal atoms in the same place, and is hence ruled out. It may also be mentioned that structure 1 would place eight metal atoms on a cube diagonal, giving a maximum metal-metal distance of 2.03 Å, which is considerably smaller than metal-metal distances observed in other crystals. Structure 2, dependent on one parameter u, has structure factors

$$S_{h00} = 16\,\overline{M} \cos 2\pi h u \text{ for } h = 2, 6, \ldots,$$
$$S_{h00} = 16\,\overline{M}\,(1 + \cos 2\pi h u) \text{ for } h = 4, 8, \ldots.$$

All values of the parameter u are eliminated by the comparisons $600 > 200$, $400 > 200$, and $10.0.0 > 200$.

There accordingly remains only structure 3. We may take $8(Mn, Fe)$ in $8e$ rather than $8i$, which leads to the same arrangements. The structure factor for various orders from (100) is then

$$S_{h00} = 8\overline{M}\,(\cos 2\pi h u - 1) \text{ for } h = 2,\ 6,\ 10, \text{ etc.}$$
$$S_{h00} = 8\overline{M}\,(\cos 2\pi h u + 3) \text{ for } h = 4,\ 8,\ 12, \text{ etc.}$$

All distinct structures are included in the parameter range $-0.25 \leqslant u \leqslant 0.25$, and, moreover, positive and negative values of u give the same intensity of reflection from $(h00)$. Hence we need consider only $0 \leqslant |u| \leqslant 0.25$. In Figure 1 are shown values of $|S|$ calculated over

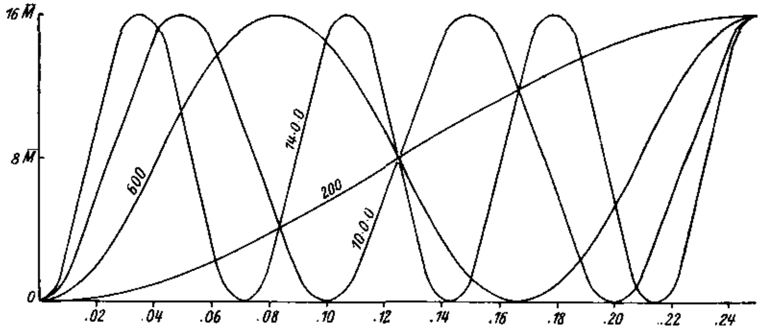

Fig. 1. Structure factor curves over the range $0 \leqslant |u| \leqslant 0.25$ with $\overline{M}$ constant.

this range with a constant value for $\overline{M}$. It is seen that the observed intensity inequality $600 > 200$ rules out the region $0.125 \leqslant |u| \leqslant 0.25$, and $10.0.0 > 200$ and $14.0.0 > 200$ further limit $|u|$ to between 0.00 and 0.06. The value of $|u|$ can be more closely determined by the use of atomic amplitude curves. The intensity of the diffracted beam can be taken as

$$I = K \cdot A_{hkl}^2, \tag{1}$$

with

$$A_{hkl} = \sum_i A_i e^{2\pi i (h x_i + k y_i + l z_i)}. \tag{2}$$

In this expression A_i, the atomic amplitude function, is given by

$$A_i = \left\{\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}\right\}^{\frac{1}{2}} \cdot F_i, \tag{3}$$

in which F_i is the atomic F-function. Values of A_{Fe} and A_O calculated for MoK_α radiation and for an average wave-length of 0.40 Å effective on Laue photographs from Bragg and West's F-curves[1]) are given in

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[1]) W. L. Bragg and J. West, Z. Krist. **69**, 118. 1928.

Table IV. Figure 2 shows values of A_{h00} for $h = 2, 4 \ldots 16$ over the range of values 0 to 0.06 for $|u|$. It is seen that the value $|u| = 0.030 \pm 0.005$ is indicated by the observed intensities of Table I.

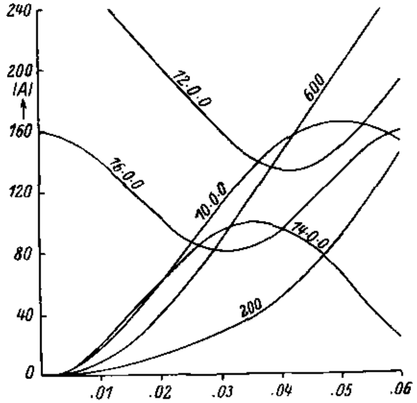

Fig. 2. A-curves over the range $0 \leqq |u| \leqq 0.06$.

Table IV.

Atomic A-values for Iron and Oxygen.

d_{hkl}	$\lambda = 0.40$ Å		$\lambda = 0.709$ Å	
	A_O	A_{Fe}	A_O	A_{Fe}
5.00 Å	28.0	79.0	21.2	59.8
2.50	14.5	45.0	10.4	33.6
1.67	7.5	30.1	5.8	21.7
1.25	4.4	21.8	3.5	15.6
1.00	2.7	16.8	2.1	11.6
0.83	1.5	12.5	1.2	9.0
0.72	0.9	10.3	0.6	7.3
0.63	0.6	8.4	0.4	5.9
0.55	0.4	6.6	0.2	4.6
0.50	0.3	5.2	0.1	4.0
0.45	—	4.5	—	3.6
0.42	—	3.7	—	3.4
0.39	—	3.1	—	3.2

Now there are two physically distinct arrangements of the metal atoms corresponding to $|u| = 0.030$, the first with $u = 0.030$, and the second with $u = -0.030$; and it is not possible to distinguish between them with the aid of the intensities of reflection of X-rays which they give. Let us consider the positions $24e$. The structure factor for $24e$ is:

$$
\begin{aligned}
S_{hkl} &= 8\overline{M}[\cos 2\pi(hu + l/4) + \cos 2\pi(ku + h/4) + \cos 2\pi(lu + k/4)] \\
&\qquad \text{for } h, k, l \text{ all even;} \\
&= 8\overline{M}\cos 2\pi(hu + l/4) \text{ for } h \text{ even, } k \text{ odd, } l \text{ odd;} \\
&= 8\overline{M}\cos 2\pi(ku + h/4) \text{ for } h \text{ odd, } k \text{ even, } l \text{ odd;} \\
&= 8\overline{M}\cos 2\pi(lu + k/4) \text{ for } h \text{ odd, } k \text{ odd, } l \text{ even.} \\
&= 0 \text{ otherwise.}
\end{aligned}
$$

It is seen that the value of the structure factor is the same for a given positive as for the same negative value of u, except for a difference in sign in some cases. But the positive and the negative parameter values correspond to structures which are not identical, but are distinctly different, as can be seen when the attempt to bring them into coincidence is made. This is a case where two distinct structures give the same intensity of X-ray reflections from all planes, so that they could not be distinguished from one another by X-ray methods. The presence of atoms in $8e$ or $8i$ does not change this result. In the case of bixbyite a knowledge of the positions of the oxygen atoms would enable the decision between these alternatives to be made, but the rigorous evaluation of the three oxygen parameters from the X-ray data cannot be carried out.

Zachariasen's arrangement of the metal atoms approximates the first of our two (that with the positive parameter value), and would be identical with it if his parameters were taken to be 0.030 and 0.530 rather than 0.021 and 0.542.

4. The Prediction and Verification of the Atomic Arrangement.

Recognizing the impracticability of determining the positions of the oxygen atoms from X-ray data, we have predicted a set of values for the oxygen parameters with the use of assumed minimum interatomic distances which is found to account satisfactorily for the observed intensities of a large number of reflections and which also leads to a structure which is physically reasonable.

The $Fe—O$ distances in hematite are 1.99 and 2.06 Å. The $(Mn, Fe)—O$ distances in bixbyite are expected to be the same in case that (Mn, Fe) has the coordination number 6, and slightly smaller, perhaps 1.90 Å, for coordination number 4. The radius of $O^{=}$ is 1.40 Å, and the average $O—O$ distance in oxide crystals has about twice this value. When coordinated polyhedra share edges the $O—O$ distance is decreased to a minimum value of 2.50 Å, shown by shared edges in rutile, anatase, brookite, corundum, hydrargillite, mica, chlorite, and other crystals. Our experience with complex ionic crystals leads us to believe that we may safely assume that the $(Mn, Fe)—O$ and the $O—O$ distances in bixbyite will not fall below 1.80 Å and 2.40 Å respectively.

On attempting to build up a structure on the basis of the first arrangement of the metal atoms, with $u = 0.030$, we found that there is no way in which the oxygen atoms can be introduced without causing interatomic distances smaller than the assumed minimum ones. This arrangement (which approximates Zachariasen's) is accordingly eliminated.

The second arrangement of the metal atoms, with $u = -0.030$, is such that satisfactory interatomic distances are obtained only when the oxygen atoms are in the general position with $x \simeq \frac{3}{8}$, $y \simeq \frac{1}{8}$, and $z \simeq \frac{3}{8}$. Each oxygen atom is then at about 2 Å from four metal atoms; if it be assumed that these four metal-oxygen distances are equal, the parameters are found to have the values

$$x = 0.385, \qquad y = 0.145, \qquad z = 0.380.$$

With this structure each metal atom is surrounded by six oxygen atoms at a distance of 2.01 Å, and the minimum $O—O$ distance is 2.50 Å. These dimensions are entirely reasonable.

It is probable that the various metal-oxygen distances are not exactly equal, but show variations of possibly ± 0.05 Å. The predicted parameter values may correspondingly be assumed to be accurate to only about ± 0.005.

Table V. Data from an Oscillation Photograph of Bixbyite[1]).

$\{h0l\}$	Estimated Intensity	$S^2/10{,}000$
202	0.00	0.01
402	0.01	0.28
404	10	67.00
602	0.2	0.68
604	0.6	1.69
802	0.2	0.74
804	2	3.34
806	0.05	0.19

The predicted structure has been verified by the comparison of the observed intensities of reflection for a large number of planes and those calculated with the use of Equation 1. Data for such comparisons for planes $(h00)$ and $(h0l)$ reflecting on oscillation photographs are given in Tables I and V, and for other planes giving Laue reflections in

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1) These reflections are from the first, second, and third layer lines of the same photograph as that from which the data of Table I were obtained, so that intercomparisons between Tables I and V may be made.

Table II. It is seen that the agreement between calculated and observed intensities is almost complete; the existent discrepancies are generally explicable as resulting from small errors in the parameter values (within the limits ± 0.005) or from errors in the assumed F-curves, for which an accuracy greater than ± 20% is not claimed.

5. Description of the Structure.

The structure found by the methods just described agrees well with the general principles underlying complex ionic crystals. The arrangement of the metal ions is shown in Fig. 3. These ions are nearly in cubic close-packing, so that the structure gives nearly the maximum dispersion of cations with given molal volume. Each cation is surrounded by six oxygen ions at a distance of 2.01 Å, at the corners of a highly distorted octahedron. These octahedra are of two types, corresponding to the two positions $8e$ and $24e$. Each $8e$ octahedron (with point-group symmetry C_{3i}) shares six edges with adjoining $24e$ octahedra, and each $24e$ octahedron shares six edges also, two with $8e$ and four with other $24e$ octahedra. Every shared edge is 2.50—2.52 Å long, in striking agreement with the minimum dimensions found in other crystals for shared edges and the theoretical values obtained for rutile and anatase[1]). These shared edges are arranged differently for $8e$ and $24e$; the distortion accompanying their shortening leads to octahedra of the shapes shown in Fig. 4 and 5. Various interatomic distances are given in Table VI.

Table VI.

Interatomic Distances in Bixbyite.

$(Fe, Mn) — O_A = 2.01$ Å	$(Fe, Mn) — O_K = 2.01$ Å	$O_A — O_F = 2.52$ Å	$O_H — O_E = 3.29$ Å
$(Fe, Mn) — O_B = 2.01$	$(Fe, Mn) — O_L = 2.01$	$O_B — O_E = 2.52$	$O_L — O_G = 3.29$
$(Fe, Mn) — O_C = 2.01$	$O_A — O_B = 3.13$	$O_B — O_F = 2.52$	$O_H — O_I = 2.50$
$(Fe, Mn) — O_D = 2.01$	$O_B — O_C = 3.13$	$O_C — O_D = 2.52$	$O_K — O_L = 2.50$
$(Fe, Mn) — O_E = 2.01$	$O_D — O_E = 3.13$	$O_C — O_E = 2.52$	$O_H — O_K = 2.51$
$(Fe, Mn) — O_F = 2.01$	$O_D — O_F = 3.13$	$O_K — O_I = 3.38$	$O_I — O_L = 2.51$
$(Fe, Mn) — O_G = 2.01$	$O_E — O_F = 3.13$	$O_G — O_E = 2.92$	$O_G — O_K = 2.50$
$(Fe, Mn) — O_H = 2.01$	$O_A — O_C = 3.13$	$O_H — O_G = 3.12$	$O_E — O_I = 2.50$
$(Fe, Mn) — O_I = 2.01$	$O_A — O_D = 2.52$	$O_L — O_E = 3.12$	

Each oxygen ion is common to four octahedra, and has $\sum_i{}' s_i = 2$, in accordance with the electrostatic valence rule.

The structure can be instructively compared with that of fluorite, CaF_2. In fluorite the calcium ions are arranged at face-centered lattice points, and each is surrounded by eight fluorine ions at cube corners.

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[1]) Linus Pauling, Z. Krist. **67**, 377. 1928.

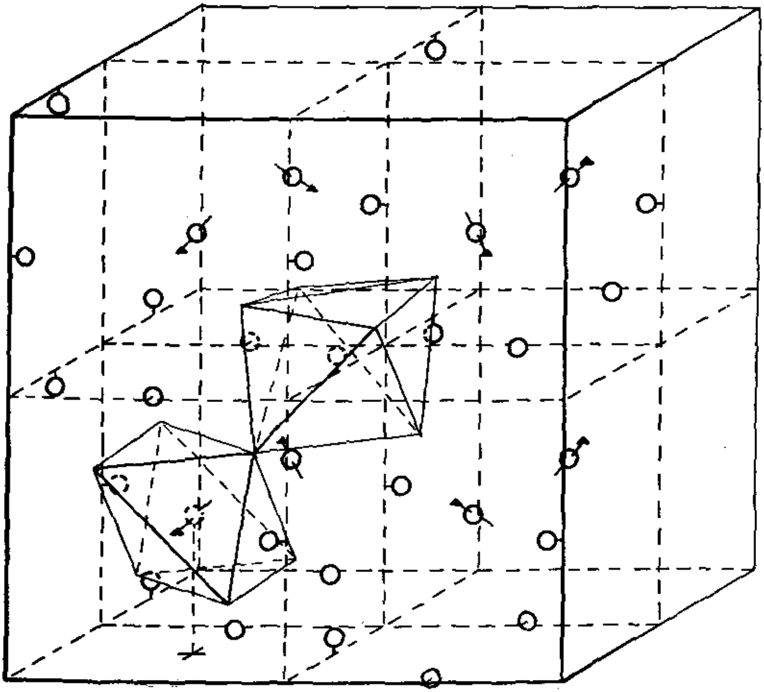

Fig. 3. The structure of bixbyite. The metal ions are shown, together with one of each kind of distorted octahedron.

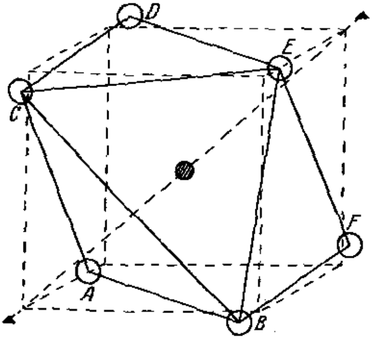

Fig. 4. The 8 *e* octahedron, showing its relation to a cube.

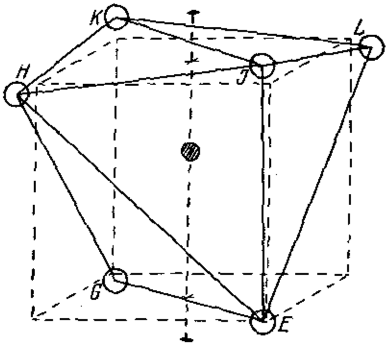

Fig. 5. The 24 *e* octahedron, showing its relation to a cube.

If one-fourth of the fluorine ions are removed and the others are replaced by oxygen ions, calcium being replaced by (*Mn*, *Fe*), a structure is obtained which approximates that of bixbyite, which differs from it only in small displacements of the ions. This similarity is shown by the fact that the highly distorted octahedra have corners which are nearly at six of the eight corners of a cube, the six being chosen differently for the $8e$ and the $24e$ octahedra, as is seen from Fig. 4 and 5. This analogy was, indeed, pointed out by Zachariasen for his incorrect structure. As a matter of fact the "ideal" structure, with $u = 0$ and $x = \frac{3}{8}$, $y = \frac{1}{8}$, $z = \frac{3}{8}$, corresponding to Zachariasen's original atomic arrangement also corresponds to ours. Zachariasen very instructively pointed out that this ideal structure lies midway between the fluorite and the sphalerite arrangements, being obtained either by removing certain anions from fluorite, or by adding anions to sphalerite, the positions of the other ions remaining unchanged in either case. With the ideal structure the coordinated polyhedra are cubes with two truncated corners; for $8e$ these corners are at the ends of a body diagonal, for $24e$ at the ends of a face diagonal. The actual structure is distorted from the ideal one, which leads to too small interionic distances, in such a way as to give a constant metal-oxygen distance and a minimum oxygen-oxygen distance (for shared edges) of 2.50 Å. In Zachariasen's arrangement the distortion was in the opposite direction.

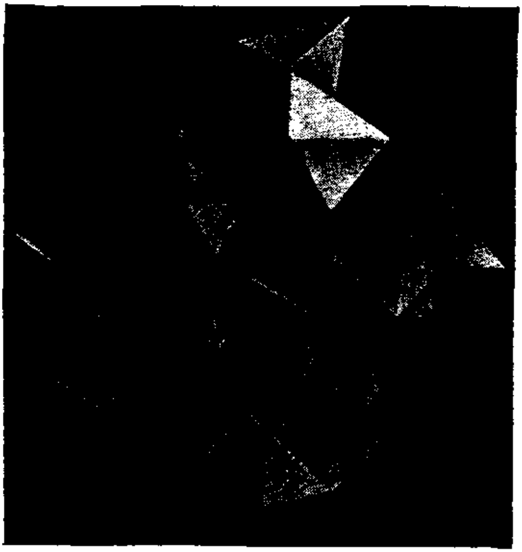

Fig. 6. A photograph of a model representing one half of the unit cube. The arrangement of the six $24e$ octahedra sharing edges with an $8e$ octahedron is clearly shown.

Table VII. Interatomic Distances in Sesquioxides.

Substance	a	$M—O$
$(Fe, Mn)_2O_3$	9.365 Å	2.01 Å
Mn_2O_3	9.41	2.02
Sc_2O_3	9.79	2.10
Y_2O_3	10.60	2.27
In_2O_3	10.12	2.17
Tl_2O_3	10.57	2.26
Sm_2O_3	10.85	2.33
Eu_2O_3	10.84	2.33
Gd_2O_3	10.79	2.32
Tb_2O_3	10.70	2.30
Dy_2O_3	10.63	2.28
Ho_2O_3	10.58	2.27
Er_2O_3	10.54	2.26
Tm_2O_3	10.52	2.26
Yb_2O_3	10.39	2.23
Lu_2O_3	10.37	2.22

As mentioned by **Zachariasen**, **Goldschmidt**[1]) found that the range of radius-ratio values leading to stability of the C-modification is about $0.60 < \frac{R_{M^{+3}}}{R_{O^{=}}} < 0.88$, which is high[2]) for a structure in which the coordination number is 6. The explanation of this is obvious; the coordinated octahedra are deformed so that the anions are nearly at six cube corners, and the radius ratio will accordingly tend to the range of values giving the coordination number 8.

A photograph of a model representing the structure is shown in Fig. 6.

Zachariasen's investigation makes it highly probable that the sesquioxides forming crystals of the C-modification have the same structure as that which we have found for bixbyite, and the similarity in intensities on powder photographs of the different substances which he reports indicates that the parameter values do not change very much throughout the series. Thus in all these crystals the cations are attributed the coordination number 6. Values of interionic distances calculated from **Zachariasen**'s values of a with the bixbyite parameters are given in Table VII. It is probable, however, that the oxygen parameters do change as a increases in such a way as to keep shared edges short, for with the bixbyite parameters the shared edges increase from 2.50 Å to about 2.90 Å in Sm_2O_3 and Eu_2O_3. As a consequence the metal-oxygen dis-

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[1]) V. M. **Goldschmidt**, »Geochem. Vert.-Ges. d. El.«, VII, p. 76.

[2]) **Linus Pauling**, J. Am. chem. Soc. **51**, 1010. 1929.

tances in Table VII are probably a little larger than the true ones, the maximum error being 0.10 Å. It is worthy of mention that the C-structure and the corundum structure correspond to nearly the same interionic distances (1.99—2.06 A in hematite as compared with 2.01 Å in bixbyite), as is to be expected from the equality in coordination number of the cation.

Summary.

With the use of data from oscillation and Laue photographs it is shown that the unit of structure of bixbyite has $a = 9.365$ Å and contains $16\,(Mn, Fe)_2O_3$. The lattice is the body-centered cubic one, Γ_c'', and the space group is T_h^7. Two possible arrangements alone of the metal atoms are found to be compatible with the X-ray data (oxygen atoms being neglected), the first with $8\,(Mn, Fe)$ in $8e$, $24\,(Mn, Fe)$ in $24e$ with $u = 0.030$, and the second the same except with $u = -0.030$. It is pointed out that these two physically distinct arrangements give the same intensities of reflection of X-rays from all planes, so that an unambiguous structure determination for a crystal containing only atoms in $24e$ (or $24e$, $8e$, $8i$) could not be made with X-ray methods alone, despite the dependence on only one parameter.

The assumption that the (Mn, Fe)—O and O—O distances can not fall below 1.80 Å and 2.40 Å, respectively, eliminates the first metal atom arrangement, for there are no positions for oxygen satisfying it. With the second arrangement of metal atoms this assumption requires $48\ O$ to be in the general position of T_h^7, with $x \cong \frac{3}{8}$, $y \cong \frac{1}{8}$, $z \cong \frac{3}{8}$. Each oxygen ion is then nearly equidistant from four cations. Making the four (Mn, Fe)—O distances equal, values of the parameters are predicted which lead to good agreement between observed and calculated intensities of reflection from a large number of planes. The structure found for bixbyite has

$8(Mn, Fe)$ in $8e$
$24(Mn, Fe)$ in $24e$ with $u = -0.030 \pm 0.005$
$48\,O$ in x, y, z, etc. with $x = 0.385 \pm 0.005$,
$y = 0.145 \pm 0.005$,
$z = 0.380 \pm 0.005$.

A description of the structure with values of interatomic distances for bixbyite and for Sc_2O_3, Mn_2O_3, Y_2O_3, In_2O_3, Tl_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3, which are shown to have the same structure by Zachariasen's investigation, is given in Section 5.

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