THE CRYSTAL STRUCTURE OF SWEDENBORGITE, $NaBe_4SbO_7$

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INTRODUCTION

The hexagonal mineral swedenborgite was first described by Aminoff[1] in 1924 as a sodium aluminum antimonate, with the following properties: colorless to light yellow, hardness about 8, axial ratio $c/a = 1.6309$, definite basal cleavage. Later Aminoff and Blix[2] reported the substance to contain beryllium instead of aluminum, its formula being $NaBe_4SbO_7$. They also suggested several possible atomic arrangements, based on their x-ray examination.

Our interest in the structure of antimonic acid and the antimonates[3] had led us in the meantime to procure specimens of the mineral and begin its study with x-rays. Using the stochastic method,[4] we formulated an atomic arrangement and tested it by a comparison of observed and calculated intensities of reflection. The structure found for swedenborgite, and described in the following pages, is identical with one of those suggested by Aminoff and Blix. Because of the ambiguity of their results, the different nature of our investigation and theirs, and the interesting type of structure found, we believe it worth while to present the following brief account of our work.

We are indebted to Professor Charles Palache of Harvard University for providing us with excellent crystals of swedenborgite, and to Dr. J. Sherman for assistance with the intensity calculations.

THE UNIT OF STRUCTURE AND SPACE GROUP

Data from oscillation photographs of the K radiation of molybdenum led to the values $a_0 = 5.47$ Å and $c_0 = 8.92$ Å for the edges of the hexagonal unit of structure, in approximate agreement with the values of Aminoff and Blix, $a_0 = 5.42$ Å and $c_0 = 8.80$ Å. This unit was found to be compatible with all reflections observed on several completely indexed Laue photographs.

[1] G. Aminoff, *Z. Kryst.*, vol. **60**, p. 262, 1924.

[2] G. Aminoff and R. Blix, *Kgl. Sv. Vet. H.*, vol. **11**, p. 3, 1933.

[3] L. Pauling, *Jour. Amer. Chem. Soc.*, vol. **55**, p. 1895, 1933.

[4] See, for example, L. Pauling, *Z. Kryst.* vol. **84**, p. 442, 1933, for a previous application of this method of crystal-structure investigation (to zunyite, $Al_{13}Si_5O_{20}(OH, F)_{18}Cl$).

(The ratio c_0/a_0 agrees with the axial ratio obtained from goniometric measurements. Aminoff reported $c/a = 1.6309$, from 36 measurements of the angle $(10 \cdot 1)(10 \cdot \bar{1})$. We found the value $27°58'17'' \pm 12''$ for the angle $(10 \cdot 0)(10 \cdot 1)$, as the average of 36 measurements; this leads to the axial ratio $c/a = 1.6308 \pm 0.0003$.)

A Laue photograph prepared with the incident beam parallel to [0001] was found to show a six-fold axis and six planes of symmetry. The point-group symmetry of the crystal is hence D_{3h}, C_{6v}, D_6, or D_{6h}. Of these, C_{6v} is indicated to be correct by Aminoff and Blix's description of one crystal of pronounced hemimorphic face development.

Of the four space groups C_{6v}^1 to C_{6v}^4, two (C_{6v}^2 and C_{6v}^3) are eliminated by numerous observed reflections of the type $(H0 \cdot L)$ with L odd. The fact that no reflections of the type $(HH \cdot L)$ with L odd were observed indicates very strongly that the correct space group is C_{6v}^4 (or, if the evidence for hemimorphy is not conclusive, possibly D_{3h}^4 or D_{6h}^4).

FORMULATION OF POSSIBLE ATOMIC ARRANGEMENTS

In formulating possible atomic arrangements we make the following assumptions, based on the rules governing the structure of complex ionic crystals[5] (swedenborgite being considered to contain bonds with sufficient ionic character to make these rules applicable). We shall for convenience use the word ions in referring to the atoms in the crystal, without signifying that the bonds are all of the extreme ionic type.

1. Each antimony ion is surrounded by six oxygen ions arranged at the corners of an approximately regular octahedron,[3] the antimony-oxygen distance being about 2.0 Å (sum of ionic radii[6] 2.02 Å, sum of covalent radii[7] 2.10 Å).

2. Each beryllium ion is surrounded by four oxygen ions arranged at the corners of an approximately regular tetrahedron, the beryllium-oxygen distance being about 1.65 Å, as in BeO.

3. Each sodium ion is surrounded by six to twelve oxygen ions, at distances greater than 2.35 Å.

4. The electrostatic valence rule is satisfied, each oxygen ion being held by electrostatic bonds with total bond strength 2.

[5] L. Pauling, *J. Am. Chem. Soc.*, vol. **51**, p. 1010, 1929.

[6] L. Pauling, *J. Am. Chem. Soc.*, vol. **49**, p. 765, 1927.

[7] L. Pauling and M. L. Huggins, *Z. Kryst.*, vol. **87**, p. 205, 1934. The octahedral radius of antimony, 1.44 Å, is assumed to be 6% greater than the tetrahedral radius.

5. Other factors being equal, the polyhedra will avoid sharing faces and edges.

The strength of a bond from antimony (Sb^{5+}) to each of its six coordinated oxygens (which we shall call O_{II} or O_{III}) is 5/6. The strength of a beryllium bond is $\frac{1}{2}$. Hence each of these oxygen ions is required by the electrostatic valence rule to be common to one antimony octahedron and two beryllium tetrahedra ($5/6 + 2 \times \frac{1}{2}$ $= 1\ 5/6$), the remaining 1/6 being made up by sodium bonds.

The seventh oxygen ion of the formula $NaBe_4SbO_7$, which we shall call O_I, is not bonded to antimony. It is accordingly common to four beryllium tetrahedra, thus satisfying the electrostatic valence rule ($4 \times \frac{1}{2} = 2$).

Our first problem is to construct a suitable framework of octahedra and tetrahedra. We have seen that this will contain groups of four tetrahedra, which have no shared edges. Such a group can be based on a cubic close-packed arrangement of twelve O_{II}'s and O_{III}'s about the central O_I, as illustrated by the group of four tetrahedra shown in Figure 1a, or on a hexagonal close-packed arrangement, as shown in Figure 1b.
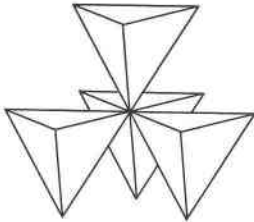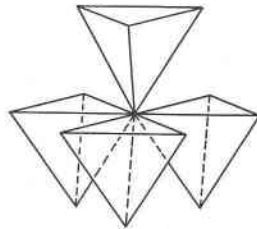

FIG. 1a   FIG. 1b

FIG. 1. Groups of four tetrahedra with a common corner, the twelve outer corners being arranged around the central one (a) as in cubic close packing and (b) as in hexagonal close packing.

It is seen that the antimony octahedra lie in the same layers as the upper tetrahedra of the groups of four shown in Figure 1; for if they were in the layers below, they would share edges with the tetrahedra. A layer of octahedra at positions required by the value of a_0 is shown in Figure 2. Each of the upper corners of octahedra is to serve as a top corner for an upper tetrahedron. The only way in which this can be achieved is shown in Figure 2a. Also each of the lower corners is to serve as top corner for two of the lower tetrahedra. This can be achieved without sharing edges in only one way, shown in Figure 2b.
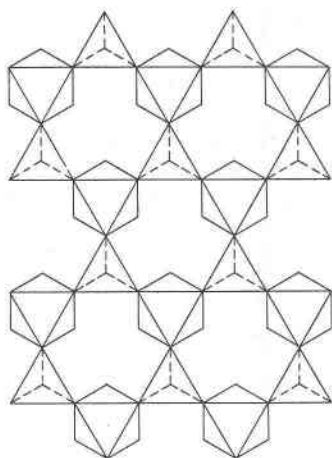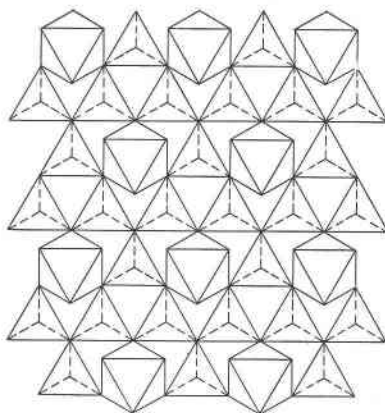
Fig. 2a   Fig. 2b

Fig. 2. Layers of polyhedra in swedenborgite. The same layer of octahedra is shown in 2a and 2b; in 2a the tetrahedra in the same layer are drawn, and in 2b the tetrahedra in the layer directly below. It is seen that the groups of four tetrahedra are of the type shown in Figure 1a, corresponding to cubic close packing.

We thus have been led to a certain sequence of atom planes, which may be described as follows. Let us designate[8] positions of upper octahedron corners by A, lower corners by C, and octahedron centers by B, using these symbols also for unoccupied close-packed positions. The sequence of atom planes determined above is
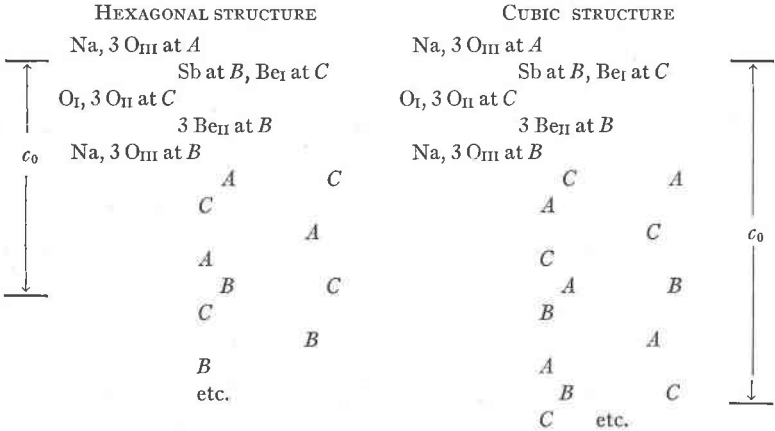
$$3O_{III} \text{ at } A$$
$$\text{Sb at } B, \text{ Be}_I \text{ at } C$$
$$1O_I \text{ and } 3O_{II} \text{ at } C$$
$$3 \text{ Be}_{II} \text{ at } B$$
$$3O_{III} \text{ at } B.$$

It is seen that oxygen atoms O_I and O_{II} are surrounded by other oxygen atoms in the way corresponding to cubic close packing.

In addition, we know that the upper octahedron corners are to serve as lower corners for the next higher layer of tetrahedra. However, this does not fix the positions of these tetrahedra, for their upper corners can occupy either positions C or positions B, the first alternative corresponding to hexagonal close-packing of oxygen atoms about O_{III} and the second to cubic close-packing.

[8] This convenient nomenclature for close-packed layers can be defined by the use of hexagonal coordinates in a plane as follows: A, $X=0$, $Y=0$; B, $X=1/3$, $Y=2/3$, and C, $X=2/3$, $Y=1/3$.

Corresponding to these alternatives we obtain two distinct but very closely related structures, represented by the following schemes.

HEXAGONAL STRUCTURE	CUBIC STRUCTURE

Na, 3 O_{III} at A | Na, 3 O_{III} at A
Sb at B, Be_I at C | Sb at B, Be_I at C
O_I, 3 O_{II} at C | O_I, 3 O_{II} at C
3 Be_{II} at B | 3 Be_{II} at B
c_0 Na, 3 O_{III} at B | Na, 3 O_{III} at B

HEXAGONAL:
```
        A       C
    C
            A
    A
        B       C
    C
            B
    B
    etc.
```

CUBIC:
```
            C       A
        A
                C       $c_0$
        C
            A       B
        B
                A
        A
        B       C
        C    etc.
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The first of these structures repeats after two layers, and so leads to a unit of the size observed for swedenborgite. It is the structure of swedenborgite. This structure is based on double hexagonal close-packing of oxygen ions, first found in brookite[9] and topaz.[10] Of the sixteen close-packed positions in the unit, only fourteen are occupied by oxygens; we place sodium ions in the other two, thus giving sodium the coordination number 12. The structure has the symmetry of space group C_{6v}^4, and the predicted values of a_0 and c_0 (based on the assumed interatomic distances) agree perfectly with the observed values. These facts, together with the agreement with general structural principles, provide strong support for the structure. Further verification is given by the agreement of observed and calculated x-ray intensities, discussed in the following section.

The second structure repeats after three layers, and, indeed, has cubic symmetry rather than hexagonal symmetry. From the standpoint of crystal chemistry this structure is not inferior to the other for the compound $NaBe_4SbO_7$, and we predict that cubic crystals of this substance may be discovered, for which the face-centered unit of structure, containing 4 $NaBe_4SbO_7$, will have $a_0 = 7.72$ Å.

[9] L. Pauling and J. H. Sturdivant, Z. Kryst., vol. 68, p. 239, 1928.
[10] L. Pauling, Proc. Nat. Acad. Sci., vol. 14, p. 603, 1928.

Verification of the Structure

In terms of the equivalent positions of space group C_{6v}^4,

$2a$: $00u$, $00\frac{1}{2}+u$;

$2b$: $\frac{1}{3}\,\frac{2}{3}u$, $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}+u$;

$6c$: $u\,\bar{u}\,v$, $2\bar{u}\,\bar{u}\,v$, $u\,2u\,v$,

   $\bar{u}\,u\,\frac{1}{2}+v$, $2u\,u\,\frac{1}{2}+v$, $\bar{u}\,2\bar{u}\,\frac{1}{2}+v$;

the ideal atomic arrangement (for regular polyhedra) can be described as follows:

2 Sb   at $2b$, $u=0$;

2 Na   at $2b$, $u=\frac{5}{8}$;

2 Be$_\mathrm{I}$ at $2a$, $u=\frac{1}{16}$;

2 O$_\mathrm{I}$ at $2a$, $u=\frac{3}{8}$;

6 Be$_\mathrm{II}$ at $6c$, $u=\frac{1}{6}$, $v=\frac{5}{16}$;

6 O$_\mathrm{II}$ at $6c$, $u=\frac{1}{2}$, $v=\frac{3}{8}$;

6 O$_\mathrm{III}$ at $6c$, $u=\frac{1}{6}$, $v=\frac{1}{8}$.

We have calculated intensities of reflection for a large number of planes on the basis of this arrangement, using the customary bath-method formula

$$I_{HI\cdot L}=\text{Constant}\cdot\frac{1+\cos^2 2\theta}{2\sin 2\theta}\,|F_{HI\cdot L}|^2,$$

with $F_{HI\cdot L}=\sum f_j e^{2\pi i(Hx_j+Iy_j+Lz_j)}$

the sum being taken over all atoms in the unit. Pauling-Sherman f-values[11] were used, and the temperature factor omitted, the error due to this omission being small for such a hard crystal. The results of the calculation are given in Table 1, for comparison with the observed intensity values on oscillation photographs. The photographs were made with the K-radiation of molybdenum filtered through zirconia, with 30° oscillation about $[1\bar{1}\cdot 0]$ through various angular regions. Estimates of intensity values were made by the visual comparison of films prepared under identical conditions except for changed time of exposure. The Ott correction was made for reflections not in the equator.

It is seen that the agreement is satisfactory, providing strong evidence that the suggested structure is correct. Further evidence is given by the fact that the ideal arrangement requires that no reflections of the type $\dfrac{H+2I}{3}$ integral, L odd occur. None such was observed on the photographs.[12]

[11] L. Pauling and J. Sherman, *Z. Kryst.*, vol. **81**, p. 1, 1932.

[12] Several reflections apparently of this type were observed on one series of photographs; it was then found that these were due to reflections from a twinned crystal We have not determined the type of twinning involved.

The number of parameters is so great that it is not practicable to attempt to determine deviations from the ideal values.

Our intensity data agree with those of Aminoff and Blix, so far as they overlap. Our structure is identical with one of those suggested by them, and found by them to be compatible with their data.

TABLE 1

CALCULATED AND OBSERVED INTENSITIES OF *X*-RAY REFLECTION
FOR SWEDENBORGITE

HI·L	*Intensity* Calculated	Observed	HI·L	*Intensity* Calculated	Observed
11·0	50	50	20·2	20	36
22·0	52	45	30·2	15	18
33·0	4.8	5	40·2	3.5	3.5
44·0	8.0	6	50·2	1.1	2
55·0	1.5	2	60·2	2.5	4
22·2	7.8	10	21·0	5.1	5
33·2	4.9	5	21·2	4.1	4
44·2	1.8	2.5	31·0	2.5	3
55·2	1.6	3	31·1	6.0	10
33·4	3.2	5	31·2	2.0	3
44·4	0.4	0.5	31·3	7.6	10
55·4	1.3	2	32·1	4.0	6
33·6	2.5	4	32·2	1.4	2
44·6	2.2	2	32·3	5.3	7
55·6	1.1	2	32·4	0.5	2
44·8	2.9	3	41·2	6.6	9
55·8	1.2	2	41·4	3.6	5
44·10	1.7	1	42·1	3.4	3
40·1	5.4	8	42·2	1.5	2
50·1	5.6	7	42·3	2.1	4
40·3	8.3	8	42·4	1.0	1.5
50·3	1.8	5	42·5	3.8	5.0
50·5	2.1	4	42·6	2.2	2
10·0	16.0	23	42·7	1.7	1
20·0	2.6	4.5	43·4	0.6	1
30·0	17.1	18.0	43·5	1.8	2
40·0	0.9	0	43·6	0.6	0.5
50·0	0.9	0	43·7	1.5	1.5
			43·8	0.8	0.5

Their other structures are of types which we eliminated early in our process of formulating a structure because of conflict with the assumed structural characteristics.

Description of the Structure

The structure of swedenborgite is shown in Figure 3. Its general nature has been discussed in the process of its formulation.

Each beryllium ion is surrounded by four oxygen ions at tetrahedron corners, the Be-O distance (for ideal parameter values) being 1.67 Å. Each antimony ion is surrounded by six oxygen ions at octahedron corners. It seems probable, in view of the predicted
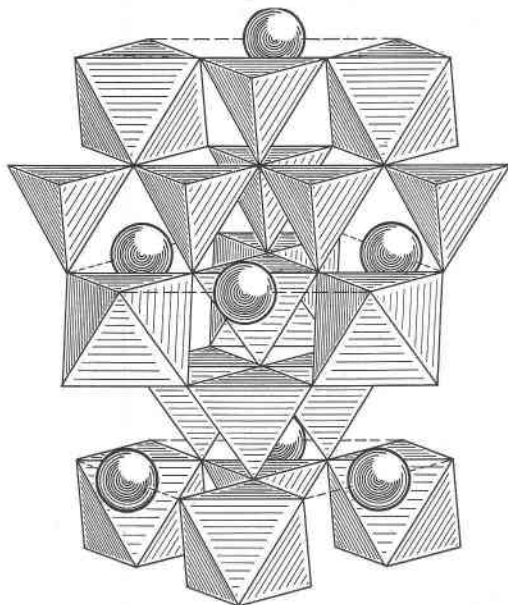

Fig. 3. A portion of the structure of swedenborgite, showing the antimony octahedra, the groups of four beryllium tetrahedra, and the sodium ions (represented by spheres). The oxygen and sodium ions together form a double hexagonal close-packed aggregate.

values 2.02–2.10 Å for the Sb-O distance, that there is some distortion of the structure, increasing the Sb-O distance somewhat above the value 1.93 Å corresponding to the ideal parameter values, and decreasing the Be-O distance to about 1.65 Å, as in beryllium oxide.

Each sodium ion is surrounded by twelve oxygen ions at about 2.7 Å, a value compatible with the radius sum 2.35 Å in view of the large coordination number.

Each O_I is reached by four beryllium bonds, of strength $\frac{1}{2}$, and each O_{II} and O_{III} by one antimony bond (5/6), two beryllium bonds

($\frac{1}{2}$), and two sodium bonds (1/12), the electrostatic valence rule thus being exactly satisfied.

The crystal provides an excellent type of structure for a complex ionic substance, illustrating most of the general rules for such structures, as discussed in an earlier section. The substance can be considered as a basic antimonate (salt of the acid H_7SbO_6) of sodium and beryllium. It bears an interesting relation to basic beryllium acetate,[13] $Be_4O(CH_3COO)_6$; in the molecules of this substance there occur four beryllium tetrahedra with one common corner, the twelve remaining corners being occupied by carboxyl oxygens, whereas in swedenborgite these twelve corners are occupied by oxygen atoms common to two tetrahedra (in different groups) and one antimonate octahedron. The chemical formula of swedenborgite might well be written as $NaBe_4OSbO_6$.

The vertical columns of tetrahedra (one of which is shown in Figure 3) form an interesting feature of the structure. It might be expected that these would cause the crystal to show prismatic cleavage. A simple consideration[14] of the number of bonds broken by cleavage along various planes shows, however, that basal cleavage is to be expected, in agreement with observation. The very strong antimony bonds will resist rupture, and the sodium bonds can be neglected. Cleavage along $(00 \cdot 1)$ requires three beryllium bonds to be broken per unit rhomb, with area $\sqrt{3}a_0^2/2$ $= 25.8$ Å^2, or 0.116 bond per Å^2, whereas for $(10 \cdot 0)$ there are four bonds per 24.4 Å^2 or 0.164 per Å^2, and for $(11 \cdot 0)$ eight bonds per 42.3 Å^2 or 0.189 per Å^2.

Summary

The hexagonal unit of swedenborgite, containing $2NaBe_4SbO_7$, has $a_0 = 5.47$ Å and $c_0 = 8.92$ Å. The atomic arrangement, in terms of the equivalent positions of space group C_{6v}^4, is the following:

2 Sb   at $2b$, $u=0$;
2 Na   at $2b$, $u=\frac{5}{8}$;
2 Be$_I$ at $2a$, $u=\frac{1}{16}$;
2 O$_I$ at $2a$, $u=\frac{3}{8}$;
6 Be$_{II}$ at $6c$, $u=\frac{1}{6}$, $v=\frac{5}{16}$;
6 O$_{II}$ at $6c$, $u=\frac{1}{2}$, $v=\frac{3}{8}$;
6 O$_{III}$ at $6c$, $u=\frac{1}{6}$, $v=\frac{1}{8}$.

[13] L. Pauling and J. Sherman, *Proc. Nat. Acad. Sci.*, vol. **20**, p. 340, 1934.

[14] For the similar discussion of cleavage of aluminosilicate crystals see L. Pauling, *Proc. Nat. Acad. Sci.*, vol. **16**, p. 453, 1930, and M. D. Shappell, *Dissertation*, California Institute of Technology, **1933**.

The crystal contains octahedral SbO_6 groups, and groups of four beryllium tetrahedra with one corner common to all four, the other corners being shared with tetrahedra of other groups and with antimony octahedra. The large oxygen and sodium ions are arranged in double hexagonal close packing.