X-RAY INVESTIGATION OF BØGGILDITE

BY

CHR. K. MØLLER

Abstract.

X-ray investigation of single crystals of Bøggildite shows that they are monoclinic and belong to space group No. 14 $P2_1/c$. The axes are a = 5.24 Å, b = 2 a = 10.48 Å, c = 18.52 Å and $\beta = 107°.35$.

The presence of weak extra layer lines is interpreted as being due to a twinning or superstructure. The external faces are (012) with its analogues.

Acknowledgement.

I am very indebted to Hans Clausen, Reader in Mineralogy at the University of Copenhagen and to Professor Dr. phil. A. Tovborg Jensen for many illuminating discussions about the above subject.

We have examined two single crystals of Bøggildite by X-rays. Already several years ago, HANS CLAUSEN, Reader in Mineralogy at the University of Copenhagen, obtained rotation diagrams of another Bøggildite crystal using CoK_α-radiation.[1] He found from these photographs the length of the axis about which the crystal was rotated to be 5.25 Å.

We have taken oscillation and WEISSENBERG diagrams of crystals rotating about two different axes with a BUERGER WEISSENBERG goniometer. Film diameter was 57.3 mm and we have used filtered CuK_α-radiation ($\lambda = 1.5418$ Å). The crystals which we used seemed to be essentially single crystals when investigated under the polarizing microscope; they were rather large, about $1 \times {}^1/_2 \times {}^1/_2$ mm, so that the intensities are affected by absorption and extinction. Fig. 1. shows an oscillation diagram taken of a crystal rotating about its morphological axis. This zone-axis we have chosen as a-axis. From the spacings of the layer lines we obtain a = 5.25 Å in perfect agreement with CLAUSEN's value. The diagram shows no plane of symmetry perpendicular to the a-axis. Hence the crystal has no mirror plane perpendicular to **a**, nor can, from Friedel's law, the a-axis be a diad axis.—Besides the main layer lines, there are some weaker ones between them corresponding to half integral values of h or to a doubling of the a-axis. The latter possibility, however, does not seem very likely because the character of these secondary layer lines is quite different from that of the others; they are somewhat irregular and the spots are weak and rather diffuse. On the first of the weak layer lines there is a comparatively strong, sharply bounded interference spot, the appearance of which makes it likely that it is due to Renninger effect[2].

The same observations can be made on CLAUSEN's oscillation diagram of Bøggildite.

The zero layer line WEISSENBERG diagram of the same crystal (fig. 2) shows two prominent slanting lines, 90° apart.

When we superpose the first, second and third layer line WEISSENBERG diagrams on the zero layer line diagram, it is seen that they also have prominent slanting lines at the same place (the connection between

the moving camera and the rotating crystal has not been loosened any time during the series of exposures). Therefore, if we choose the above-mentioned two slanting lines of the zero layer line as preliminary reciprocal axes b_1^* and c_1^* we can obtain an orthorhombic reciprocal lattice, and hence, also, an orthorhombic direct lattice. Using the relation $2d \sin \vartheta = n\lambda$ we obtain from the zero layer line WEISSENBERG diagram the direct, orthorhombic axes

$$a_1 = 5.25 \text{ Å} \qquad b_1 = 10.48 \text{ Å} \qquad c_1 = 17.65 \text{ Å}$$

With orthorhombic indexing, it is observed that reflexions $h_1 0 l_1$ are absent for $h_1 + l_1$ odd, and $0 k_1 0$ are absent for k_1 odd, furthermore that reflexions of the type $h_1 k_1 0$ are rather weak for h_1 odd. But no orthorhombic space group has this combination of absent reflexions, nor does orthorhombic symmetry comply with the results of microscopic examination of the crystals in polarized light: The faces $(0 k_1 l_1)$ do not show symmetrical extinction as expected for an orthorhombic crystal. However, it is possible to choose a set of monoclinic axes so that the monoclinic indices hkl are related to the orthorhombic indices $h_1 k_1 l_1$ by the following relations:

$$h = h_1 \qquad k = k_1 \qquad l = h_1 + l_1$$

This corresponds to the following transformation of the orthorhombic axes to monoclinic axes:

$$\mathbf{a} = \mathbf{a}_1 \qquad \mathbf{b} = \mathbf{b}_1 \qquad \mathbf{c} = \mathbf{a}_1 + \mathbf{c}_1$$

and consequently the monoclinic axes and angle are:

$$a = 5.25 \text{ Å} \qquad b = 10.48 \text{ Å} \qquad c = 18.42 \text{ Å} \qquad \beta = 106°.5$$

where $\operatorname{tg}(180 - \beta) = \dfrac{a_1^*}{c_1^*} = \dfrac{c_1}{a_1} = 3.36_5$. The uncertainty on the axes is estimated not to be larger than 1 %, and the angle β should be accurate to $\pm 1°$.

It may easily be seen that the condition for the monoclinic reciprocal lattice points hkl to coincide with those of an orthorhombic net $h_1 k_1 l_1$ is: $-\cos \beta = \dfrac{c^*}{a^*} = \dfrac{a}{c}$. With monoclinic indexing, the absent reflexions are: h0l for l odd and 0k0 for k odd, corresponding to space group No. 14 $P2_1/c$. Oscillation and WEISSENBERG diagrams have also been taken of a crystal rotating about its b-axis which bisected the

angle between two external prism faces. The axes obtained from these diagrams are in complete agreement with the above results, and h0l is absent for l odd (monoclinic description) as may be seen on the zero-layer line diagram of h0l (fig. 3).

Hence from the systematic absences of reflexions: h0l absent for l odd, 0k0 absent for k odd, it is concluded that the crystals are monoclinic with space group No. 14 $P2_1/c$ (Int. Tab. for X-Ray Cryst. 1952) and this seems the only one to be considered. There are four equivalent general positions, and two equivalent special positions in the unit cell of this space group.

The volume of the unit cell with the above axes is $972 \cdot 10^{-24}$ cm^3. The density of the crystal has been determined [3] to be 3.66 g/cm^3, hence the weight of the unit cell contents is $356 \cdot 10^{-23}$g. From chemical analysis a molecular weight of 543.3 has been found[4]. We then calculate that there are 3.95 = 4 molecules per unit cell. All that can be said then, is that the number of molecules calculated per unit cell is in agreement with the space group symmetry, but so far no conslusions can be drawn about atomic parameters on this basis.

The weak extra layer lines which appear when the crystals rotate about the a-axis may be explained as being due to some kind of superstructure or to twin formation with [121] as twin axis, or (121) as twin plane. In the orthorhombic description of the lattice, this direction has indices [120] and bisects the angle between the orthorhombic $\mathbf{a}_1$- and $\mathbf{b}_1$-axes, and it may easily be seen from a drawing of the reciprocal $(\mathbf{a}_1\mathbf{b}_1)$-plane, that a twin formation of this kind will produce extra layer lines midway between those already presemt when, as here, $a_1 = \frac{1}{2} b_1$.

Powder diagrams have been taken of Bøggildite in a Guinier camera first with monochromatized CuK_α-radiation, then, as the diagram turned out to be rather complex also with CrK_α-radiation[1] ($\lambda = 2.2909$ Å).

It does not seem possible to index these diagrams on an orthorhombic $\mathbf{a}_1\mathbf{b}_1\mathbf{c}_1$-net, but if it is assumed that the angle between $\mathbf{a}_1$ and $\mathbf{c}_1$ is 89°.1 instead of 90° all powder lines can be accounted for. The measured and calculated $\sin^2\vartheta$-values for CrK_α-radiation are given in table 1 together with the monoclinic indices h k l and the visually estimated intensities (NaCl was admixed to the specimen to give some calibration marks.) Although a completely unambiguous indexing cannot be achieved above ϑ = c. 30° it is thought that the values of the axes and the angle are more accurate than those derived from the WEISSENBERG diagrams:

$$a = \frac{1}{2} b = 5.24 \text{ Å} \qquad c = 18.52 \text{ Å} \qquad \beta = 107°.35$$

[1]) We are indebted to Professor G. HÄGG, Uppsala, and his staff for the Cr-diagram.

Table 1. Observed and calculated $\sin^2\vartheta$-values of Bøggildite for CrK_α-radiation.

Indices hkl	Intensity	$\sin^2\vartheta$ obs.	$\sin^2\vartheta$ calc.	Remarks
002	(v) w	0.0168	0.0167	..
012	w	0.0287	0.0286	..
020	m-v	0.0476	0.0476	..
$11\bar{2}$	(v) w	0.0631	0.0633	..
022	(v) w	0.0648	0.0643	..
$10\bar{4}$	m-s	0.0836	0.0839	..
102	s	0.0865	0.0866	..
$12\bar{2}$	m-w	0.0988	0.0990	..
120	m-w	0.0998	0.0999	..
024	w	0.1143	0.1145	..
015	v. w.	0.1161	0.1164	..
032 111 NaCl	m-w	0.1239	0.1238	..
$12\bar{4}$	v. s.	0.1311	0.1315	..
122	m-s	0.1341	0.1342	..
$10\bar{6}$ 006	v. w.	0.1496	0.1499 0.1505	diffuse
104	v. w.	0.1541	0.1544	..
$13\bar{2}$	m	0.1582	0.1585	..
130	m	0.1596	0.1594	..
$11\bar{6}$	m-w	0.1612	0.1618	..
016	w	0.1618	0.1624	..
200 NaCl	m	0.1651	0.1650	..
114	w	0.1663	0.1663	..
034	m	0.1739	0.1740	..
$20\bar{2}$ 040	m-s	0.1900	0.1904	..
026	m	0.1980	0.1981	..
$11\bar{7}$	v. w	0.2071	0.2073	..
115	v. w	0.2126	0.2127	..
210	v. w	0.2209	0.2208	..
133	v. w	0.2235	0.2234	..
043	v. w	0.2280	0.2280	..
211	w	0.2421	0.2426	..
$22\bar{4}$	m	0.2523	0.2529	..
141 106	m	0.2554	0.2556	..
220	m-w	0.2562	0.2565	..
$13\bar{6}$ 044	m	0.2571	0.2570 0.2573	.. ..
$11\bar{8}$ 134	w	0.2607	0.2612 0.2615	diffuse

A crystal which had been adjusted for X-ray investigation with the b-axis as rotation axis, was also examined on an optical goniometer. Although its faces gave very poor, diffuse images, the angle between one of them and the b-axis could be measured: $40° 48' \pm 30'$ (all the external faces are parallel to the a-axis and hence of the type (0kl)). The angle between the (012) plane and the b-axis is given by $\text{tg}\, u = \frac{c}{2b} =$ 0.878 or $u = 41° 18'$. Considering the uncertainty on the measurement, it seems reasonable to conclude that the external faces are (012) with its analogues.

REFERENCES

1. H. Clausen. Unpublished work.
2. See e. g. H. Lipson and W. Cochran. The Crystalline State III p. 30 (Bell and Sons, London, 1953).
3. Rich. Bøgvad. Medd. Dansk Geol. For. **12** p. 109 (1951).
4. A. H. Nielsen. Acta Chem. Scand. **8** p. 136 (1954).

Færdig fra trykkeriet den 15. marts 1956.

PLATES

Plate 1.

Fig. 1. Oscillation diagram of Bøggildite. Crystal rotated about the a-axis.

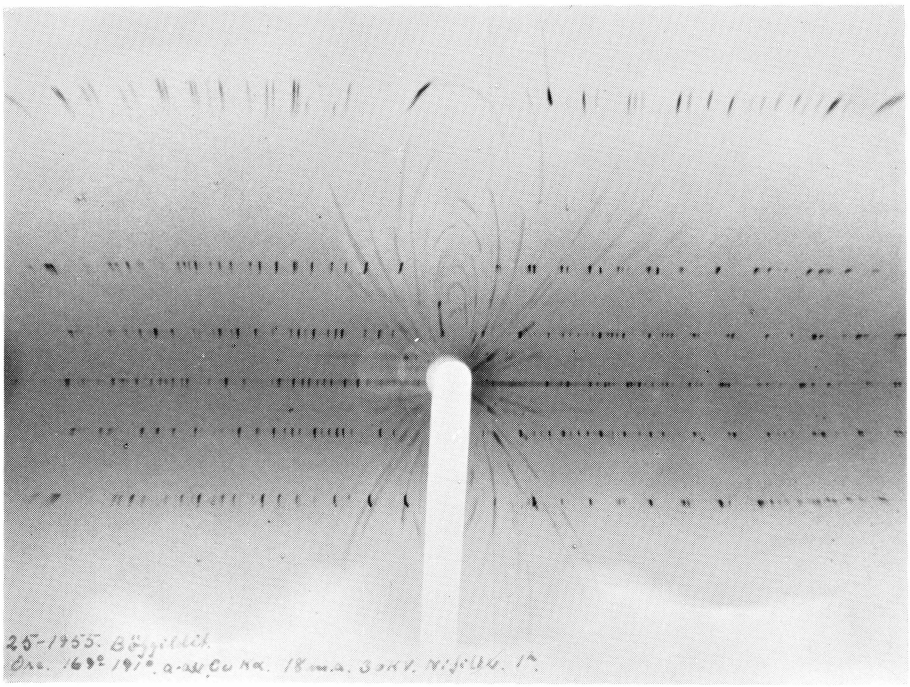

Fig. 1.

Plate 2.

Fig. 2. Zero layer line diagram of Bøggildite. Crystal rotated about the a-axis.

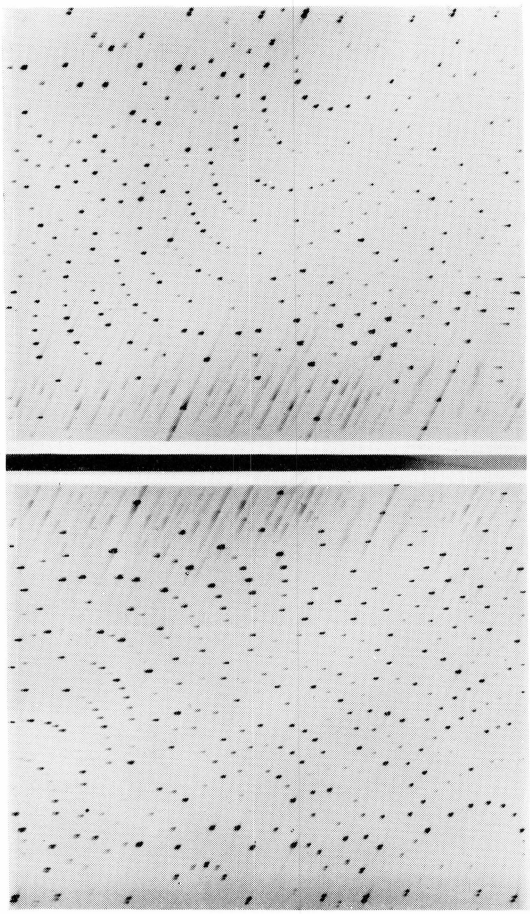

Fig. 2.

Plate 3.

Fig. 3. Zero layer line diagram of Bøggildite. Crystal rotated about the b-axis.
Fig. 4. Powder diagram of Bøggildite taken in a Guinier camera with CuK_{α}-radiation.

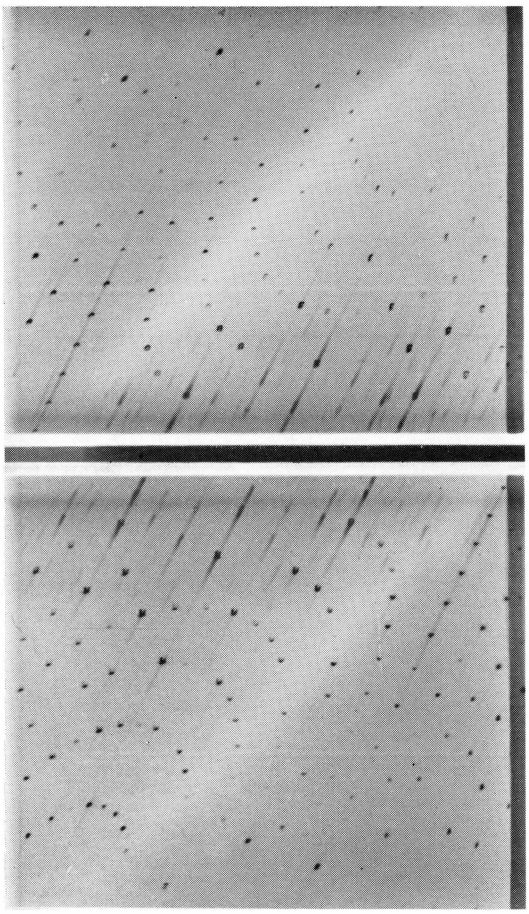

Fig. 3.

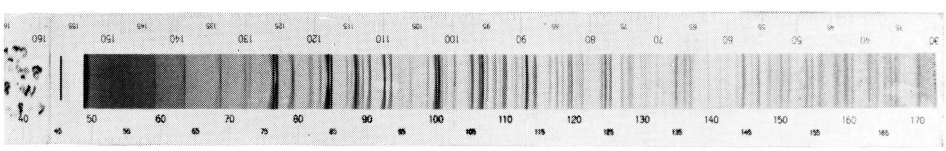

Fig. 4.