ON THE SYMMETRY AND CRYSTAL STRUCTURE OF BORNITE

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ABSTRACT

Analysis of rotation and Weissenberg photographs of a single crystal of bornite from the Carn Brea Mine, Illogan, Cornwall, has led to the conclusion that the crystal structure of bornite is not strictly isometric, but is pseudo-isometric, and is approximated by an arrangement in a cubic cell of edge-length 5.47 Å of four sulfur atoms at 000, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, with four copper or iron atoms statistically distributed over the positions $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, and two copper or iron atoms statistically distributed over the positions $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, the total number of copper atoms in the cell being five and the total number of iron atoms being one on the average.

Although bornite usually occurs in nature in aggregates of anhedral grains, a few euhedral crystals have been found. These have cubic, dodecahedral, and more rarely octahedral habit.[1] In polished surfaces under the microscope most specimens of bornite appear to be isotropic, but some exhibit weak anisotropism.[2] The observation of this weak anisotropism suggested to Professor M. N. Short[3] that bornite is not truly isometric, but merely pseudo-isometric.

The crystal structure of bornite has been investigated by *x*-ray methods by de Jong[4] and by Lundqvist and Westgren.[5] The structure deduced by de Jong is in marked disaccord with the observed intensities, as stated by Lundqvist and Westgren.[6] The cubic unit cell of edge-length 10.91 kX[7] which de Jong determined, was, however, confirmed by Lundqvist and Westgren. de Jong made a single crystal rotation photograph in addition to a powder photograph; Lundqvist and Westgren based their conclusions solely on powder photographs.

It was noted by one of us some time ago that not all the lines of two

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[1] Palache, C., Berman, H., and Frondel, C., Dana's System of Mineralogy, Seventh Edition, New York (1944), vol. 1, p. 195.

[2] Short, M. N., Microscopic Determination of the Ore Minerals: *U. S. Geol. Survey, Bull.* **825** (1931), p. 76. Schneiderhöhn, H., and Ramdohr, P., Lehrbuch der Erzmikroskopie, Berlin (1931) vol. **2**, p. 336.

[3] Oral communication.

[4] de Jong, W., Over de kristalstructuren van arsenopyriet, borniet en tetraëdriet; *Doctoral Thesis*, Delft (**1928**).

[5] Lundqvist, D., and Westgren, A., *Arkiv för kemi, mineralogie och geologi*, **12B, 1–6** (1936).

[6] The line calculated by de Jong to have the third greatest intensity (66 on the scale in which 100 represents the greatest intensity) is actually not present at all on our Weissenberg photographs.

[7] The value given by de Jong was probably in kX units although labelled in Å units.

powder photographs of bornite made with cobalt K-radiation filtered through iron foil could be indexed on the basis of the cubic unit cell of de Jong and of Lundqvist and Westgren. For this reason a rotation photograph and a set of equi-inclination Weissenberg photographs were made[8] of a single crystal of bornite from the Carn Brea Mine, Illogan, Cornwall, kindly furnished by Professor M. A. Peacock of the University of Toronto. The rotation photograph shows strong zero, sixth and twelfth layer-lines, and weak second, third, fourth, eighth, ninth and tenth layer-lines; the first, fifth, seventh and eleventh layer-lines are absent. The crystal was rotated about a "cube" edge and the identity period along this axis was calculated from the separations of the layer-lines to be 32.8 Å ± 0.1 Å,[9] that is, three times greater than the length of the cell-edge of de Jong and of Lundqvist and Westgren. Point-by-point constructions of the reciprocal lattice layers corresponding to all the equi-inclination Weissenberg photographs were carried out by the method of Schneider.[10] The reciprocal lattice layers have axes making angles of ninety degrees and with the same unit-length as that obtained by taking the reciprocal of the identity period along the rotation axis. The axes thus exhibit cubic symmetry. All the diffraction spots on the Weissenberg photographs of strong and medium intensity, as well as part of the spots of weak intensity, can be indexed in terms of the cubic cell of edge-length 32.8 Å; there are in addition, however, very many weak spots on some of the layer-lines that cannot be indexed in terms of any cell that we could find any basis for assuming. Moreover, the distribution of many of the weak spots is not in accord with isometric symmetry.

All the spots of strong and medium intensity can also be indexed in terms of a cubic cell of edge-length 5.47 Å ($=\frac{1}{6}\times 32.8$ Å). The observed intensities of the spots on the Weissenberg photographs that would result from planes in a structure with this cubic cell are listed in Table 1. With the exception of three weak spots, namely, those with indices 100, 300 and 102, all have all odd or all even indices, indicating an approximation toward a face-centered cell. If such a cell is assumed as the unit cell of a structure approximating that of bornite, its content must be taken as Cu_5FeS_4. A structure with four copper or iron atoms distributed statistically over the positions $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, two copper or iron atoms being distributed statistically over the positions $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, the total number of copper atoms in the cell being five and the

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[8] This work was carried out in the Geophysical Laboratory of the Carnegie Institution of Washington while the senior author was a member of the staff.

[9] Value based on the weighted average wave-length of cobalt $K\alpha_1$ and $K\alpha_2$ 1.790 Å.

[10] *Zeit. Krist.*, **69**, 41–48 (1928).

TABLE 1

Observed and calculated intensities of diffraction spots of a single crystal of bornite on Weissenberg photographs. The indices refer to a cubic cell of edge-length 5.47Å (not the true unit cell). Numerous weak spots occur on some of the Weissenberg photographs that cannot be indexed on the basis of this cell; however, all the spots of medium and strong intensity can be so indexed and are listed in this table.

hkl	$I_{\text{obs.}}$	$I_{\text{calc.}}$	*hkl*	$I_{\text{obs.}}$	$I_{\text{calc.}}$	*hkl*	$I_{\text{obs.}}$	$I_{\text{calc.}}$
100	w*	0	101	—*	0	102	w*	0
200	st	53	201	—	0	202	st	100
300	w	0	301	—	0	302	—	0
400	st	46	401	—	0	402	w	9
500	—	0	501	—	0	112	—	0
110	—	0	111	st	37	212	—	0
210	—	0	211	—	0	312	—	0
310	—	0	311	m	9	412	—	0
410	—	0	411	—	0	122	—	0
510	—	0	511	m	6	222	m	15
120	—	0	121	—	0	322	—	0
220	st	100	221	—	0	422	st	41
320	—	0	321	—	0	132	—	0
420	w	9	421	—	0	232	—	0
520	—	0	521	—	0	432	—	0
130	—	0	131	m	9	142	—	0
230	—	0	231	—	0	242	st	41
330	—	0	331	w	5			
430	—	0	431	—	0			
140	—	0	531	m	14			
240	w	9	141	—	0			
340	—	0	241	—	0			
440	st	68	341	—	0			
			441	—	0			
			151	m	6			
			251	—	0			
			351	m	14			

* Denotation of symbols: st strong, m medium, w weak, — not present.

total number of iron atoms being one on the average, and four sulfur atoms on the positions 000, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, yields calculated intensities for all the strong and medium spots in good agreement with those observed, as is shown in Table 1; such a structure gives small calculated intensities for some of the weak spots and zero calculated intensities for the remainder of the weak spots.[11]

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[11] An equal statistical distribution of the copper and iron atoms on the eight positions $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ gives calculated intensities in markedly less good

Lundqvist and Westgren determined the edge-length of a cubic cell for bornite to be 10.93kX.[12] Such a cell would contain 40 copper atoms, 8 iron atoms and 32 sulfur atoms. The positions of the sulfur atoms in this cubic cell are given by Lundqvist and Westgren as 32(*e*) with $x=-\frac{1}{8}$; these positions are the same as those of the sulfur atoms in the approximate structure found by us. Lundqvist and Westgren concluded that the eight iron atoms occupy the eight positions of 8(*a*), and twenty-four of the forty copper atoms occupy twenty-four of the forty-eight positions of 48(*f*) with $y=\frac{1}{4}$. These are part of the positions in which iron and copper atoms are assumed by us to be statistically distributed in the approximate structure. The calculated intensities of Lundqvist and Westgren are based on this atomic arrangement leaving out the remaining sixteen atoms of copper; they are in less good agreement with the observed intensities than are the intensities calculated from our approximate structure. Lundqvist and Westgren discussed possible locations of the omitted sixteen copper atoms and concluded that not many of them could be in the sixteenfold positions 16(*c*) and 16(*d*).[13] They stated that no matter how these sixteen copper atoms are distributed on the three positions (16(*c*), 16(*d*) and 96(*g*)), in combination with the atoms already placed, they would make the lines 422, 442, and 642[14] appear. There is no trace of any of these lines on our Weissenberg photographs, although the planes were in positions to diffract.

Since the scattering powers of copper and iron atoms differ very little, accurate values of observed intensities and careful calculations would be required to discriminate the positions of the copper and iron atoms. Our work thus far does not establish the nature of the deviations from our approximate structure. The many weak spots not accounted for indicate that bornite at ordinary temperatures is less disordered than the approximate structure that we found will account for the intensities of the strong and medium spots (as well as part of the weak spots).

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agreement with those observed than the unequal distribution adopted as the approximate structure. In the case of the artificial phase $Cu_{1.8}S$ at 170° Rahlfs came to a similar conclusion (Rahlfs, P., *Zeit. physik. Chem.*, **31B**, 157–194, 1936). It is not surprising that the approximate structure of bornite and the structure of $Cu_{1.8}S$ at 170° are similar in view of the fact that Merwin and Lombard found that at temperatures from about 500° to about 1000° a solid solution extends from pure copper sulfide to compositions considerably richer in iron than Cu_5FeS_4 (Merwin, H. E., and Lombard, R. H., *Economic Geology*, **32**, 203–284, 1937).

[12] The value was given in Å units, but was probably in kX units.

[13] Lundqvist and Westgren suggested, however, that copper atoms might be located in these positions, which are in the centers of sulphur octahedra, and be oscillating with considerable amplitudes, in which case they would scatter with less intensities.

[14] The indices would be 211, 221, 321, referred to the cell of 5.47 Å edge-length.

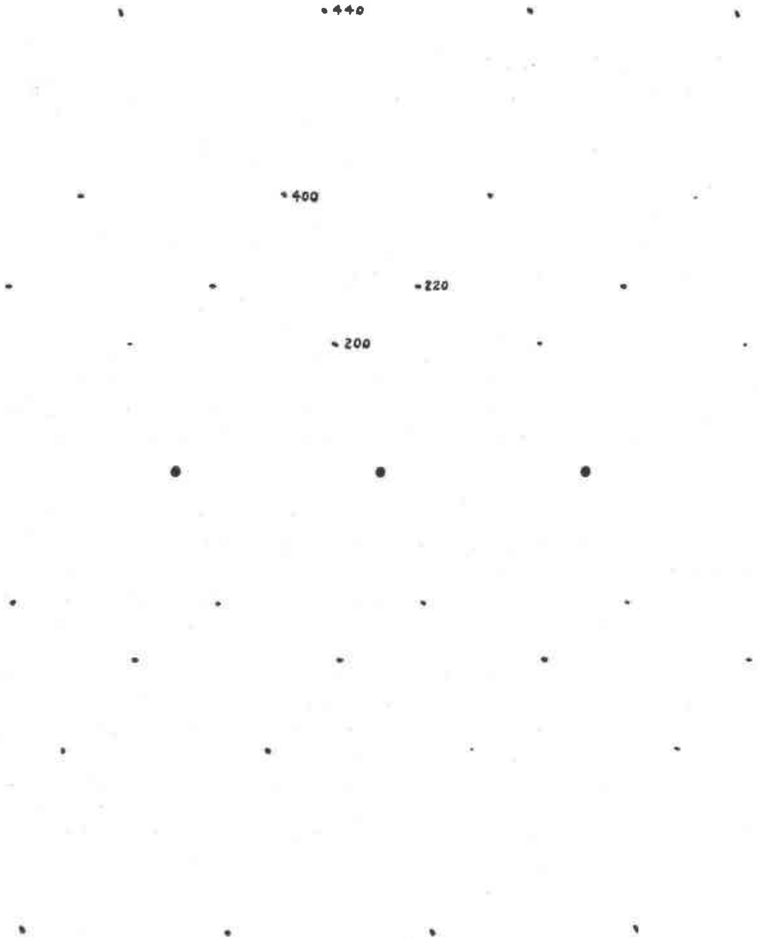

FIG. 1. Weissenberg photograph of the zero layer-line of a single crystal of bornite made with cobalt Kα-radiation. The direct beam spots along the center-line of the photograph indicate the translations of the film corresponding to 90° of rotation of the crystal. The small light areas in the centers of the direct beam spots mark the outline of the crystal. The indices of the spots refer to the cubic cell of edge-length 5.47 Å.

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[*] *Note added July 21, 1949.* Shortly after the manuscript of this paper was submitted to the editor of *The American Mineralogist,* a paper entitled "Disorder in bornite, Cu_5FeS_4"

was read before the Meeting of the Crystallographic Society of America at Ann Arbor, Michigan, by A. J. Frueh, Jr. A copy of the abstract of Dr. Frueh's paper was kindly sent to us by the editor of *The American Mineralogist.* Since Dr. Frueh determined different unit cell dimensions for the ordered form of bornite existing at ordinary temperatures from those determined by us, we sent him a copy of our manuscript and a print of one of our rotation photographs. He in turn kindly wrote us and sent us prints of several of his rotation photographs. It thus became certain that bornite of two different ordered forms exists at Illogan, Cornwall, where our crystals originated, and at Bristol, Connecticut, where Dr. Frueh's crystals were formed. The results of Dr. Frueh's investigation of bornite, which constitute a part of a more general study, will appear in *The American Mineralogist.* In view of the fact that he has investigated bornite crystals from Bristol, not only in the natural ordered state, but also in the disordered state following heating and quenching, we should emphasize that we have only made *x*-ray photographs of our crystals from Illogan in the natural ordered state, and hence we cannot say what their structure would be in the disordered state after heating and quenching; it would be reasonable to assume that our "approximate structure" might be closely related to the disordered structure of the crystals from Illogan that would result from heating and quenching, and this hypothesis should be tested.

The existence of two different ordered forms of bornite in nature raises the question whether or not their compositions also differ. A polished surface of some of our crystals from Illogan showed the presence of a little chalcopyrite, chalcocite and covellite; consequently we are not able to determine the exact composition of our bornite by analysis. However, Allen has analyzed bornites from several different localities, the purity in each case having been established by mineralographic study, and he found that the composition in all cases was very close to Cu_5FeS_4; after reviewing the literature he concluded that there is no satisfactory evidence that natural bornite varies appreciably from this formula (*Am. Jour. Sci.*, (4), **41**, 409–413 (1916)). Murdoch states that "the mineralographic examination of polished surfaces of bornite from at least 30 different localities has revealed only an exceedingly slight variation in color (Microscopical Determination of Opaque Minerals, New York, 1916, page 35). The bornite crystals studied by Dr. Frueh and those investigated by us therefore probably have a composition close to Cu_5FeS_4, but the possibility of a slight difference in composition, with which the difference in structure might be connected, is not excluded.