

## POLYMORPHISM IN BORNITE

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### ABSTRACT

Synthetic  $\text{Cu}_5\text{FeS}_4$  and natural bornite were observed in three crystalline modifications: (1) a high-temperature form, face-centered cubic, with  $a = 5.50 \pm 0.01 \text{ \AA}$ ,  $Z = 1$ , and probably anti-fluorite structure; (2) a metastable form, cubic,  $Fd\bar{3}m$  or  $F\bar{4}3m$ , with  $a = 10.94 \pm 0.02 \text{ \AA}$ ,  $Z = 8$ ; (3) a low-temperature form, primitive tetragonal, space group  $P\bar{4}2_1c$ , pseudo- $I\bar{4}2d$ , with  $a = 10.94 \pm 0.02$ ,  $c = 21.88 \pm 0.04 \text{ \AA}$ ,  $Z = 16$ . The high-temperature form is nonquenchable and is stable only above  $228^\circ \pm 5^\circ \text{ C}$ . (for synthetic materials). The metastable form appears on rapid cooling from temperatures above that of the polymorphic inversion; it changes to the low-temperature form slowly at room temperature. The low-temperature and the metastable forms are closely related in crystal structure as shown by their similar intensity distributions in  $x$ -ray patterns. Twinning of the tetragonal form about a three-fold twin axis [221] accounts for other previously reported "modifications."

### INTRODUCTION

Bornite is a common and widespread mineral occurring in numerous important copper deposits in considerable amounts. It forms under a variety of geological conditions and has been found in basic intrusives and disseminated in basic rocks, in contact metamorphic deposits in certain pegmatites and quartz veins, and even in monzonitic dikes and porphyries. It is usually found in aggregates of anhedral grains and only rarely in euhedral crystals. Previous studies of euhedral crystals indicated the existence of several polymorphs of bornite. The relationships between the various forms, however, remained almost entirely unknown. The purpose of this investigation is to study the polymorphism in both natural and synthetic bornites.

### PREVIOUS STUDIES

#### *Composition*

Bornite has been recognized as a mineral since 1725. Its chemical composition was established by Harrington (1903) and confirmed by Allen (1916) and later by Zies and Merwin (1955). The analyses by these workers are the only ones, to our knowledge, that have been performed on pure materials. The mineral composition obtained from these analyses is  $\text{Cu}_5\text{FeS}_4$  within the limits of error of the analytical methods.

At elevated temperatures, however, bornite forms extensive solid solution with numerous sulfide-type minerals, and its composition therefore

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often is significantly different from  $\text{Cu}_5\text{FeS}_4$  at the time of mineral formation. On cooling, exsolution takes place, as is shown by the fine textures (such as chalcocite, chalcopyrite, and digenite lamellae) that occur in many bornites (Laney, 1911; Schwartz, 1931, 1939; Latsky, 1942; Kullerud, Donnay, and Donnay, 1960). Thus the structure of bornite, which at elevated temperatures tolerates variations in the Cu:Fe and metals:S ratios, shows a strong tendency, on slow cooling, to expel foreign atoms by exsolution and thus to bring the composition back to  $\text{Cu}_5\text{FeS}_4$ .

### *Crystallography*

The first attempt to determine the crystal structure of bornite by  $x$ -ray diffraction methods was made by de Jong (1928). He reported a unit cell of cubic symmetry, with  $a = 10.910 \pm 0.005$  kX, on natural bornite from Cornwall, England. The structure suggested by de Jong, however, did not account for the observed intensities. Lundqvist and Westgren (1936) studied synthetic bornite by means of powder photographs. They proposed a cubic structure, with  $a = 10.93$  kX and space group  $Fd\bar{3}m$ , in which the sulfur atoms are arranged in cubic close packing with the metal atoms situated in the interstices. Several schemes for distributing the metal atoms were suggested, but none could be confirmed by  $x$ -ray intensity data. Tunell and Adams (1949) examined crystals of "bornite" from the Carn Brea Mine, Illogan, Cornwall, and reported a unit cell of cubic symmetry with  $a = 32.8 \pm 0.1$  Å. They proposed an approximate structure, giving reasonable intensities to all strong and medium reflections, based on a cubic sub-cell with  $a = 5.47$  Å. A considerable number of weak reflections, however, were not accounted for. The very same specimens studied by Tunell and Adams (1949) were recently re-examined in polished sections and by  $x$ -ray precession photographs by Morimoto, Greig, and Tunell (1960) and found to consist of three phases.

Frueh (1950) investigated bornite crystals from Bristol, Connecticut, and from Butte, Montana, and produced  $x$ -ray, thermal, and electrical evidence indicating that bornite can exist in both a low- and a high-temperature form. Frueh considers the structural difference between the forms to be one of order-disorder. The disorder becomes measurable at  $170^\circ$  C. and reaches completion at  $220^\circ$  C. For the low-temperature form, Frueh (1950) reports orthorhombic symmetry with  $a = b = 21.94$  Å and  $c = 10.97$  Å. He later informed us, however (priv. comm., July 28, 1958), that he had been dealing with a "multiple crystal." Quoting him: "The reason it was called orthorhombic was that the intensity of reflections did not show four-fold symmetry. From the smaller fragment it appears to be truly tetragonal with  $a = 10.97$  and  $c = 21.94$  Å." Frueh (1950) reports that, after being heated at about  $220^\circ$  C. and then chilled rapidly in ice

cold water, the bornite crystals possess cubic symmetry with  $a = 10.97 \text{ \AA}$ .\* He concludes that the high or disordered form is retained by rapid chilling, in other words that it is quenchable.

Kullerud and Roseboom (1958) confirm the existence of two forms of bornite and give the inversion temperature as about  $190^\circ \text{ C}$ . for bornite coexisting with digenite along the  $\text{Cu}_9\text{S}_5\text{-Cu}_5\text{FeS}_4$  join.

Kullerud, Donnay, and Donnay (1960) report two forms of bornite in a hand specimen from Coppercorp Mine in Ontario, Canada. One form is cubic with  $a = 21.94 \pm 0.06 \text{ \AA}$  and diffraction aspect  $P^{***}$ . The other has a primitive orthorhombic lattice, with pseudotetragonal cell dimensions:  $a = b = 21.90 \pm 0.06 \text{ \AA}$ ,  $c = 10.95 \pm 0.03 \text{ \AA}$ , in agreement with the low-temperature bornite described by Frueh (1950).

#### SYNTHETIC BORNITE

Bornite was synthesized by holding mixtures of copper, iron, and sulfur (of required composition) at fixed temperatures for various periods of time. The technique employed involves the use of rigid silica tubes. The products were chilled rapidly in cold water and identified at room temperature by optical and  $x$ -ray methods. Some of the bornite single crystals grown in this way were later investigated at elevated temperatures by Buerger's  $x$ -ray precession method.

#### *Starting Materials*

Bornite of  $\text{Cu}_5\text{FeS}_4$  composition was grown from mixtures of the elements without catalytic agents or additional components. Experiments were carried out using copper, iron, and sulfur in the ratios 5:1:4. Since the vapor pressure of bornite of  $\text{Cu}_5\text{FeS}_4$  composition even at  $1000^\circ \text{ C}$ . is very low (Merwin and Lombard, 1937), the loss of sulfur and of metals to the vapor was negligible for the volume of free space allowed.

The copper was obtained from the American Smelting and Refining Company, ASARCO grade A-58. The analysis of this material shows it to consist of 99.999+ per cent Cu. No impurities are detectable by spectrographic analysis. The sum of selenium and sulfur is less than 1 ppm ( $<0.0001$  per cent) by chemical analysis. This material was received as cast copper rods  $\frac{3}{8}$  inch in diameter. Copper for each experiment was obtained by meticulous filing to avoid contamination. The grain size of these filings was about 0.5 to 1 mm. Reaction rates were high so further reduction in size was unnecessary.

The iron was obtained from the National Bureau of Standards, Standard sample 55, open-hearth iron. A chemical analysis of this material,

\* This form is produced metastably during the cooling period, as will be shown later in this paper.

which contains 99.84 per cent Fe, is given by Kullerud and Yoder (1959).

The sulfur was of the same material as that used by Kullerud and Yoder (1959); it contains only 0.007 per cent impurity, all of which is carbonaceous material.

### *Equipment*

All experiments were carried out in evacuated silica-glass tubes in the manner described by Kullerud (1953). The free space within the tube was reduced as described by Kullerud and Yoder (1959). The tubes were heated in regulated furnaces at temperatures accurate to  $\pm 2^\circ$  C. The outside wall of the tube was at 1 atm; no external supporting pressure medium was employed. The vapor pressure inside the tube containing a mixture of copper, iron, and sulfur in the 5:1:4 ratios reaches its maximum shortly after the tube has been placed in the hot furnace, because the temperature in the tube then rises rapidly (toward that of the furnace) and the vapor pressure over each element\* increases with temperature. Some reaction will take place between the elements in the tube but, even when the temperature of the furnace has been reached, liquid sulfur is still present. At this point the pressure inside the tube can be estimated from the pure sulfur vapor pressure curve (Kullerud and Yoder, 1959). Thus, if the furnace temperature is  $750^\circ$  C. the pressure in the tube is about 25 atm. Free sulfur is consumed by the reaction with the metals and soon the liquid sulfur is gone. From then on the vapor is not saturated, and the vapor pressure decreases gradually until equilibrium is obtained in the tube. The vapor pressure over bornite of  $\text{Cu}_5\text{FeS}_4$  composition, according to Merwin and Lombard, is about 400 mm Hg at  $750^\circ$  C. This initially high pressure may be sufficient to cause an explosion if the tube is heated much above  $750^\circ$  C. before the free sulfur has been consumed. For this reason each tube was first heated at  $700^\circ$  C. until all free sulfur had combined with the metals, which normally took less than 12 hours. Then the tube was extracted from the furnace and opened under acetone to avoid oxidation before and during the process of grinding. The fine homogeneous powder, while still covered by acetone, was placed in a new silica tube, which then was evacuated and sealed.

### *Quench Procedure*

The silica tubes were removed from the furnace with tongs and plunged into water as quickly as possible at the termination of each experiment. Thus room temperature was reached in a few seconds. It was found that the form of bornite that is stable at elevated temperatures cannot be retained even by the most rapid chilling, thus quenching of this form is not

\* The vapor pressures of copper and iron are negligible compared with that of sulfur.

possible. However, the rate of chilling, although never fast enough to produce a truly quenched phase, does influence the nature of the product. The effects of chilling are given later.

#### *Description of the $\text{Cu}_5\text{FeS}_4$ Phase*

The products obtained in silica tube experiments are identified by their physical, optical, and  $x$ -ray properties. Since bornite was synthesized in a two-step operation, the products of the first step, which lasted less than 24 hours, were identified by these methods in a number of experiments. The phases that are produced in addition to bornite are found as a non-equilibrium mixture of chalcopyrite, pyrrhotite, pyrite, and iron-rich chalcocite. These phases form a metastable assemblage and disappear on continued heating, even without grinding. However, grinding to a fine powder under a nonoxidizing medium shortens the time required for the establishment of equilibrium on further heating and greatly stimulates the growth of single crystals. Heating the finely ground material in evacuated silica tubes at  $900^\circ\text{C}$ . for 96 hours and then chilling it rapidly results in homogeneous  $\text{Cu}_5\text{FeS}_4$  crystals. Examination under the binocular microscope shows that the cube is the predominant form. The cube edge ranges in length from 0.05 to about 0.5 mm. The "staircase" indentations replacing cube edges in natural bornite (Kullerud, Donnay, and Donnay, 1960) are common features also in these synthetic crystals. When inspected through the transparent wall of the unopened silica tubes, the crystals are seen to possess a brassy yellow or tombac color. However, on opening the tube in air, the color changes immediately owing to a reaction between the bornite and the atmosphere. Thus, after only a few seconds, the material appears pinkish, then changes through brownish purple and purple to an iridescent blue, identical with that seen on natural bornite (Kullerud, Donnay, and Donnay, 1960). Crushing the synthetic material under acetone, after it has been allowed to turn blue on exposure to air, demonstrates that the decoloration is a surface phenomenon. The fresh surfaces, developed by the crushing and while the material is submerged, show the original brassy yellow color observed inside the unopened tubes.

In polished sections bornite of  $\text{Cu}_5\text{FeS}_4$  composition shows a pinkish or slightly orange color immediately after completion of the polishing process. However, owing to oxidation the color changes rapidly to purple and later to bluish violet. Bornite appears isotropic in polished sections after having been chilled from elevated temperatures. However, the same bornite appears slightly anisotropic when it is re-examined, after the necessary repolishing, a few weeks later.

In  $x$ -ray powder diffraction the freshly chilled material gives the cubic

bornite pattern, whereas the material re-examined several weeks later gives the pattern of tetragonal bornite. These patterns will be given by Yund and Kullerud (in preparation).

#### NATURAL BORNITE

We examined bornite crystals from four localities: (1) Coppercorp Mine, Ontario, Canada (collected by G. Kullerud); (2) Mt. Con Mine, Butte, Montana (obtained from G. Tunell); (3) Centerville, Virginia\* (obtained from the U. S. National Museum, Washington, D. C., specimen No. 106724); (4) Carn Brea Mine, Illogan, Cornwall (obtained from the U. S. National Museum, Washington, D. C., specimen No. C-525).

#### X-RAY STUDIES

The Buerger precession method was used extensively and the Weissenberg and oscillation methods were used on a number of occasions, during the investigations of synthetic and natural bornites. The *x*-ray targets were Fe, Cu, and Mo, with  $K\alpha$  wavelengths: Fe = 1.9373, Cu = 1.5418, and Mo = 0.7107 Å.

Because of the reported high-low inversion in bornite (Frueh, 1950; Kullerud and Roseboom, 1958), it was desirable to study the crystals not only below but also above the inversion temperature. The Buerger precession camera was modified to permit heating of the crystal during exposure. Thus it became routine to obtain precession photographs of bornite crystals at 300° to 400° C. The camera modification, which is described in detail by Morimoto and England (1960), may be summarized as follows. A small circular radiant-type platinum strip furnace is attached to the camera collimator. The crystal is mounted with epoxy cement on the junction of a (28 gauge) chromel-alumel thermocouple. The thermocouple wires are fastened to a fibre pin for mounting in the goniometer head. The temperature of the crystal during exposure fluctuates, partly because of limited furnace control, partly because of the movement of the crystal inside the furnace. The total variation in this specific furnace depends on the temperature control, on the angle  $\mu$ , and on the furnace temperature. Thus at 200° C. with  $\mu = 20^\circ$  the temperature variation does not exceed  $\pm 3^\circ$  C. over a 30-minute period. Good photographs are obtained in 5 to 10 minutes with molybdenum radiation (50 KV, 20 mA).

In this technique the mounted crystals are heated in air; therefore, ex-

\* Some of the bornite crystals from Centerville, Virginia, are partly covered by calcite. The crystal surface in contact with calcite has a yellow, brassy color very similar to that of the quenched synthetic materials; the surface exposed to the air shows the well-known blue iridescent bornite color.

treme caution is required. The first  $x$ -ray photograph of each crystal was made at room temperature. After rapid heating the next photograph was made in 5 to 10 minutes at the desired temperature. Then the crystal was cooled rapidly and a third exposure was made, again at room temperature. A final exposure was made after storing the crystals in air at room temperature for 2 days. The first and last photographs of each crystal were identical, indicating that oxidation, although it produced surface decoloration, did not affect the crystal structure sufficiently to be detected by  $x$ -rays.

### Polymorphism

Synthetic  $\text{Cu}_5\text{FeS}_4$  single crystals from a number of experiments were reheated in the unopened tubes at various temperatures and for various lengths of time as indicated in Table 1. After each reheating the tubes were chilled in cold water. As noted in Table 1, bornite crystals chilled from  $230^\circ\text{C}$ . or higher temperatures are of the "2a" type when studied at room temperature. Bornite crystals chilled from  $226^\circ$  and  $220^\circ\text{C}$ . are of the "modified 2a" type when studied at room temperature. The "2a"

TABLE 1. TYPES OF CRYSTALS OF SYNTHETIC BORNITE, OF  $\text{Cu}_5\text{FeS}_4$  COMPOSITION, GROWN AT  $900^\circ\text{C}$ ., COOLED, REHEATED TO AND CHILLED FROM VARIOUS TEMPERATURES, THEN STUDIED AT ROOM TEMPERATURE

Temperature of reheating, in $^\circ\text{C}$ .	Time, in hours of reheating	Types of chilled crystals	Remarks
900	21	2a	Crystals have rounded edges and show no striation.
800	73	2a	Crystals have rounded edges and show no striation.
725	116	2a	Crystals have rounded edges and show no striation.
700	55	2a	No rounded edges. Some striation on {110}. Stepwise growth on {111}.
600	70	2a	No rounded edges. Some striation on {110}. Stepwise growth on {111}.
500	168	2a	No rounded edges. Some striation on {110}. Stepwise growth on {111}.
400	454	2a	No rounded edges. Some striation on {110}. Stepwise growth on {111}.
300	187	2a	No rounded edges. Some striation on {110}. Stepwise growth on {111}.
230	310	2a	Sharp edges, striation.
226	75	Modified 2a	Sharp edges, striation.
220	200	Modified 2a	Sharp edges, striation.

type crystals have a face-centered cubic cell with  $a = 10.94 \pm 0.02 \text{ \AA}$  and space group  $Fd\bar{3}m$  or  $F\bar{4}3m$ . The "modified 2a" type crystals have a primitive cubic cell with  $a = 21.88 \pm 0.1 \text{ \AA}$ . Synthetic bornite thus appears to show two polymorphic modifications: a "high-temperature" form (2a) and a "low-temperature" form (modified 2a). The transition temperature, as can be seen from Table 1, lies between  $226^\circ \pm 3^\circ$  and  $230^\circ \pm 3^\circ \text{ C.}$ , *i.e.* at  $228^\circ \pm 5^\circ \text{ C.}$  On re-examination, at various times after the chilling process, it was found that at room temperature the "high form" changes to the "low form" in a few days, whether the crystals are stored under atmospheric conditions or in vacuum. Both forms have also been reported from natural material: the "high form" is identical with the high-temperature polymorph that Frueh (1950) obtained by heating crystals from Bristol, Connecticut; the "low form" was observed in some of the bornite crystals from Coppercorp Mine, Ontario (Kullerud, Donnay, and Donnay, 1960). Since non-quenchable modifications are common in sulfides of the Cu—S and Cu—Fe—S systems, the possibility of phase changes in quench-type experiments even during the most rapid chilling could not be discounted without careful investigations. Both synthetic and natural crystals were studied at elevated temperatures by the method described above.

*Synthetic crystals.*— $\text{Cu}_5\text{FeS}_4$  crystals, synthesized at  $900^\circ \text{ C.}$ , later heated at  $400^\circ \text{ C.}$  for 454 hours and then chilled, were studied by the precession method (Fig. 1). Photographs of  $(100)_1^*$  were taken without the screen attachment. The photograph given in Fig. 1a was taken at room temperature of material that, after rapid cooling from  $400^\circ \text{ C.}$ , was kept in vacuum for 1 week before exposure. Figure 1b shows the same material at  $240 \pm 3^\circ \text{ C.}$ , and Fig. 1c shows the material within minutes after

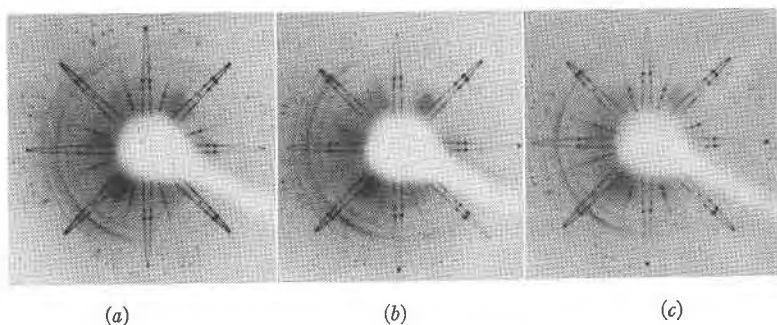


FIG. 1. High-temperature experiments on synthetic bornite. Precession photographs of  $(100)_1^*$  taken without screen attachment: (a) at room temperature 1 week after rapid cooling from  $400^\circ \text{ C.}$ , (b) at  $240 \pm 5^\circ \text{ C.}$ , and (c) at room temperature within a few minutes after (b). The changes in the patterns are schematically shown in Fig. 2.



being cooled to room temperature again. Figure 2 gives schematical diagrams, with indexed reflections, of the photographs of Fig. 1. It is noted from Figs. 1*a* and 2*a* that the unheated material possesses the low-temperature bornite form with an apparently primitive cubic cell of the "modified 2*a*" type with  $a=21.88 \text{ \AA}$ . However, this cell, as will be discussed later, is the result of twinning of a tetragonal cell having  $a=10.94 \text{ \AA}$  and  $c=21.88 \text{ \AA}$ . It is noted from Figs. 1*b* and 2*b* that at  $240^\circ \pm 3^\circ \text{ C}$ . bornite has a face-centered cubic cell with  $a=5.50 \text{ \AA}$ . Figures 1*c* and 2*c*

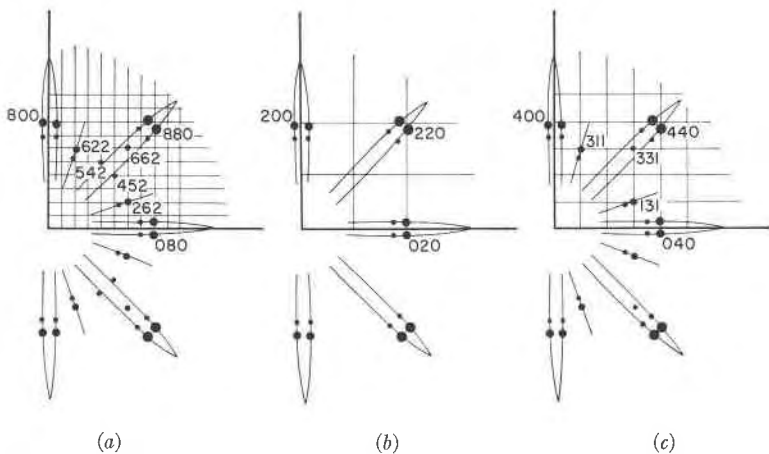


FIG. 2. Precession diagrams of Fig. 1, with reciprocal nets and index reflections.

show that at room temperature rapidly cooled bornite, at least shortly after being chilled, has the face-centered cubic cell, with  $a=10.94 \text{ \AA}$ , of the 2*a* type. Re-examination of this material, after it had been stored in vacuum for 2 days, shows transformation to the low-temperature cubic form with  $a=21.88 \text{ \AA}$ . It follows that the 2*a* cubic form must form during the chilling process and is metastable.

*Natural crystals.*—A bornite crystal from the Carn Brea Mine was likewise investigated by the modified precession method. Before heating, this crystal gives the pattern of the low-temperature form. At  $205^\circ \pm 5^\circ \text{ C}$ . the pattern is that of the high-temperature form,\* cubic with  $a=5.47 \text{ \AA}$ . When quickly cooled to room temperature this material, when investigated within a few hours after cooling, shows the metastable form, cubic with  $a=10.94 \text{ \AA}$ . Re-examination of this crystal after 4 days again

\* This bornite is associated with chalcopyrite and is not of exact  $\text{Cu}_3\text{FeS}_4$  composition. For this reason inversion to the high form takes place below  $228^\circ \pm 5^\circ \text{ C}$ ., the inversion temperature of stoichiometric  $\text{Cu}_3\text{FeS}_4$ .

showed inversion to the low-temperature cubic form with  $a = 21.88 \text{ \AA}$ .

Thus the high and low polymorphic forms as well as the metastable form occur both in synthetic bornite, of  $\text{Cu}_5\text{FeS}_4$  composition, and in natural bornite.

In order to obtain real single crystals of the low-temperature form, natural crystals from the Coppercorp Mine were heated for 8 months at  $150^\circ \text{C}$ . in evacuated silica tubes. These crystals were then found to have tetragonal symmetry with  $a = 10.94 \pm 0.02 \text{ \AA}$  and  $c = 21.88 \pm 0.04 \text{ \AA}$ . The space group was determined without ambiguity as  $P4_2c$  from the systematic extinctions or reflections. If weak reflections are neglected, the approximate space group is  $I4_2d$ .

X-ray patterns of "single" crystals of bornite from the four localities listed above show considerable variations, from one crystal to another, in the relative intensities of the reflections. None of the crystals studied gave the tetragonal patterns observed in the heated specimen from Coppercorp Mine. The intensity variations imply different symmetries and even different cell dimensions. Such changes in symmetry and in cell dimensions can be explained only as being due to twinning of individuals with varying volumes.

All the experimental data obtained on "single" crystals of natural bornite are accounted for by twinning about a three-fold twin axis [221], where the indices refer to the tetragonal cell. Figure 3 shows the inferred twin in stereographic projection. Five distinct cases of simulated symmetry and cell dimensions can be recognized, in terms of the volume fractions of the individual crystals in the twin. They are listed in Table 2.

The various symmetries and cell dimensions of natural bornites re-

TABLE 2. FIVE CASES OF SYMMETRY AND CELL DIMENSIONS THAT CAN BE SIMULATED BY THE INFERRED BORNITE TWIN

Case	Volumes of individuals			Apparent symmetry	Apparent cell dimensions, $\text{\AA}$			Observer
	Crystal I	Crystal II	Crystal III		$a$	$b$	$c$	
Twin 1	$u$	$u$	$u$	cubic	21.88	—	—	Donnay, Donnay, and Kullerud (1958)
2	$u$	$v$	$v$	tetragonal	21.88	—	21.88	
3	$u$	$v$	$w$	orthorhombic	21.88	21.88	21.88	
4	—	$u$	$u$	tetragonal	21.88	—	10.94	
5	$u$	$v$	—	orthorhombic	21.88	21.88	10.94	
Single crystal	$u$	—	—	tetragonal	10.94	10.94	21.88	Morimoto and Kullerud (1960); Frueh (priv. comm., 1958)

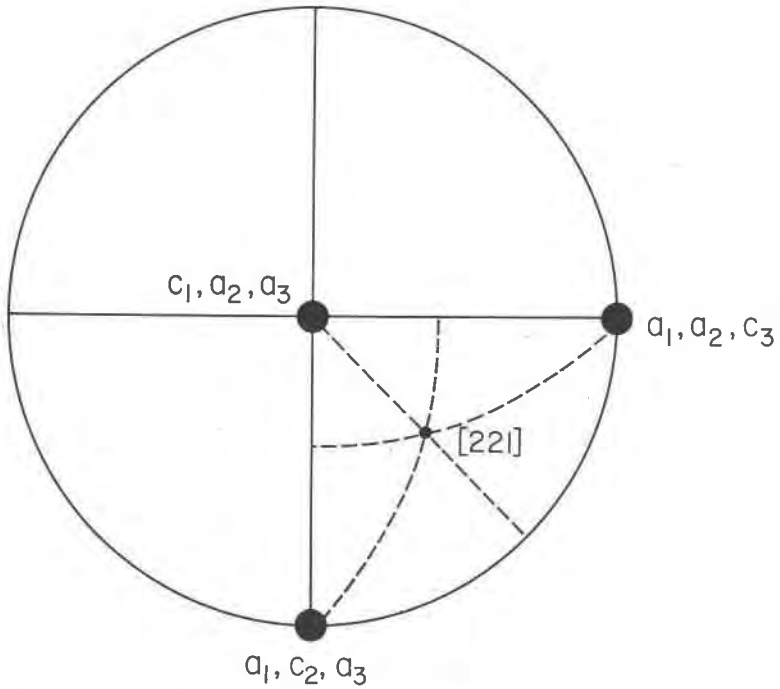


FIG. 3. Inferred bornite twin in stereographic projection. Three tetragonal crystals, I ( $a_1, c_1$ ), II ( $a_2, c_2$ ), and III ( $a_3, c_3$ ), are related by a three-fold twin axis  $[221]$ .

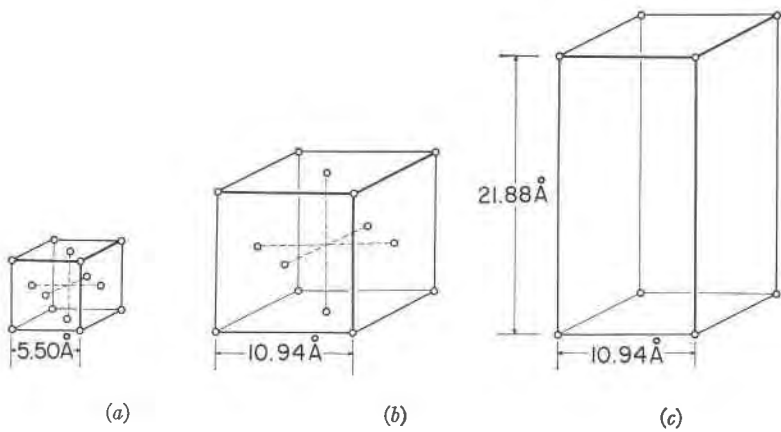


FIG. 4. Direct-lattice cells of the three forms of bornite: (a) high-temperature form, cubic; (b) metastable form, cubic; and (c) low-temperature form, tetragonal.

ported in the literature can now be easily understood as resulting from the inferred twinning. The low-temperature form of synthetic bornite with a primitive cubic cell of  $a=21.88 \text{ \AA}$ , referred to above as the "modified  $2a$ " form, is also explained as a twin of three individuals with equal volumes. It is of particular interest to note here that twinning of tetragonal crystals may raise the symmetry to cubic, keep it tetragonal, or lower it to orthorhombic. These observations once more refute the notion that twinning always increases the symmetry of crystals, a "vague and mystical idea" the fallacy of which was already demonstrated by Friedel (1926).

The direct-lattice cells of the three polymorphic forms of bornite are shown on Fig. 4. The high-temperature form seems to have the anti-fluorite structure where metal atoms are statistically distributed. The low-temperature and the metastable forms must be closely related in crystal structure because of their similar intensity distributions. Their structural relationships will be discussed in a separate paper.

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#### REFERENCES

- ALLEN, E. T. (1916), The composition of natural bornite. *Am. J. Sci.*, **41**, 409-413.
- DONNAY, G., DONNAY, J. D. H., AND KULLERUD, G. (1958), Bornite. *Carnegie Inst. Wash. Year Book*, **57**, 248-249.
- FRIEDEL, G. (1926), *Leçons de Cristallographie*, Paris, Berger-Levrault, p. 466.
- FRUEH, A. J., JR. (1950), Disorder in the mineral bornite,  $\text{Cu}_5\text{FeS}_4$ . *Am. Mineral.*, **35**, 185-192.
- HARRINGTON, B. J. (1903), On the formula of bornite. *Am. J. Sci.*, **16**, 151-154.
- DE JONG, W. (1928), *Over de kristalstructuren van arsenopyriet, borniet en tetraëdriet*. Doctoral thesis, Delft, 25 pp.
- KULLERUD, G. (1953), The FeS-ZnS system: a geological thermometer. *Norsk geol. tidsskrift*, **32**, 61-147.
- KULLERUD, G., DONNAY, G., AND DONNAY, J. D. H. (1960), A second find of euhedral bornite crystals on barite. *Am. Mineral.*, **45**, 1062-1068.
- KULLERUD, G., AND ROSEBOOM, E. H., JR. (1958),  $\text{Cu}_5\text{S}_6$ - $\text{Cu}_3\text{FeS}_4$  system. *Bull. Geol. Soc. Am.*, **69**, 1602.
- KULLERUD, G., AND YODER, H. S. (1959), Pyrite stability relations in the Fe-S system, *Econ. Geol.*, **54**, 533-572.
- LANEY, F. B. (1911), The relations of bornite and chalcocite in the copper ores of Virgilia District of North Carolina and Virginia. *Econ. Geol.*, **6**, 399-411.

- LATSKY, R. (1942), The magmatic copper ores of Namaqualand. *Trans. Geol. Soc. S. Africa*, **45**, 137.
- LUNDQVIST, D., AND WESTGREN, A. (1936), On the crystal structure of bornite. *Arkiv for Kemi, Mineralogi och Geologi*, **12B**, No. 23, 1-6.
- MERWIN, H. E., AND LOMBARD, R. H. (1937), The system Cu—Fe—S. *Econ. Geol.*, Suppl. to **32**, 203-284.
- MORIMOTO, N., AND ENGLAND, J. L. (1960), High-temperature Buerger precession camera. *Carnegie Inst. Wash. Year Book*, **59**, 175.
- MORIMOTO, N., GREIG, J. W., AND TUNELL, G. (1960), Re-examination of a bornite from the Carn Brea Mine, Cornwall. *Carnegie Inst. Wash. Year Book*, **59**, 122-126.
- MORIMOTO, N., AND KULLERUD, G. (1960), Crystallography of the  $\text{Cu}_9\text{S}_6\text{-Cu}_5\text{FeS}_4$  series. *Carnegie Inst. Wash. Year Book*, **59**, 116-122.
- SCHWARTZ, G. M. (1931), Intergrowth of bornite and chalcopyrite. *Econ. Geol.*, **26**, 186-201.
- SCHWARTZ, G. M. (1939), Significance of bornite-chalcopyrite microtextures. *Econ. Geol.*, **34**, 399-418.
- TUNELL, G., AND ADAMS, C. E. (1949), On the symmetry and crystal structure of bornite. *Am. Mineral.*, **34**, 824-829.
- ZIES, E. G., AND MERWIN, H. E. (1955), Analysis of Hamley bornite from South Australia. *Am. Mineral.*, **40**, 1001-1003.

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