

## ON THE TRANSITION OF BORNITE

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### ABSTRACT

Three polymorphs were confirmed for synthetic and natural bornite: a high-temperature form with a cubic cell of  $a=5.50 \text{ \AA}$ , a metastable form with a cubic cell of  $a=10.94 \text{ \AA}$ , and a low-temperature form with a tetragonal cell of  $a=10.94 \text{ \AA}$  and  $c=21.88 \text{ \AA}$ . The crystal structures of the high-temperature form and the metastable form were studied by  $x$ -ray single-crystal methods in order to elucidate the transition mechanisms of bornite.

The transition of bornite from the high-temperature form to the metastable form takes place by an ordering of the metal atoms. A single crystal with its metal atoms in a mobile state changes to many domains with a low symmetry, without changing the face-centered lattice of the sulfur atoms. These domains are in twin relations and collectively give a diffraction aspect of higher symmetry. The transition from the metastable form to the low-temperature form is also discussed.

### INTRODUCTION

The existence of three polymorphs of bornite was confirmed (Morimoto and Kullerud, 1961). These are a high-temperature form, a transitional metastable form, and a low-temperature form. The high-temperature form occurs in face-centered cubic crystals, with  $a=5.50 \text{ \AA}$ , diffraction aspect  $F^{***}$ ; the transitional metastable form occurs in face-centered cubic pseudocrystals, with  $a=10.94 \text{ \AA}$ , diffraction aspect  $Fd^{**}$ ; and the low-temperature form occurs in primitive tetragonal pseudocrystals, with  $a=10.94 \text{ \AA}$ ,  $c=21.88 \text{ \AA}$ , space group  $P4_2/c$ . The term "pseudocrystals" is used to designate very finely twinned edifices that simulate single crystals.

Various cell dimensions and symmetries, found in natural bornite, are explained by twinning of the low-temperature form, the twin operation being a  $120^\circ$  rotation about the row  $[221]$  of the tetragonal lattice (the body diagonal of the cubic cell).

The high-temperature form of bornite is unquenchable. When it is cooled below  $230^\circ \pm 5^\circ \text{ C}$ . it instantly changes to the metastable form. The metastable form gradually transforms to the low-temperature form at room temperature.

The easy transitions between polymorphs and the simple relations between their unit cells suggest that the three structures are closely related. In this paper the transitions between polymorphs are discussed from the structural viewpoint.

### CRYSTAL STRUCTURE OF THE HIGH-TEMPERATURE FORM

The crystal structure of the high-temperature form was determined by using single-crystal  $x$ -ray data, which were obtained at  $240^\circ \pm 5^\circ \text{ C}$ . (Morimoto, in preparation).

The crystal structure is essentially the anti-fluorite structure, only slightly more complicated. The sulfur atoms occupy the nodes of the cubic face-centered lattice, being cubically close-packed. Each tetrahedron of sulfur atoms, on the average, contains  $\frac{3}{4}$  of a metal atom. This fractional atom is itself statistically distributed over twenty-four equivalent sites inside the sulfur tetrahedron. No distinction between Cu and Fe atoms could be made. Thus, in the whole unit cell, six metal atoms are statistically distributed over  $24 \times 8 = 192$  sites. This can be considered a kind of "mobile" state of metal atoms in the cubic close-packing of sulfur atoms. The properties of bornite at high temperatures, such as high conductivity, wide range of solid solution, etc., are well understood on the basis of this dynamic state of the metal atoms in the high-temperature form.

### CRYSTAL STRUCTURE OF THE METASTABLE FORM

The metastable form is a transitional state between the high-temperature form and the low-temperature form. The crystal structure of the metastable form is, therefore, the key to the understanding of the transition mechanism.

The metastable form shows two characteristics: (a) the existence of a cubic sub-cell with  $a=5.47 \text{ \AA}$  and (b) a special extinction rule that only reflections with indices  $(4m \pm l, 4n \pm l, l)$  appear.

It was tried in vain to find a *single-crystal* structure that would account for the observed cubic reflections. The nature of the pseudocrystal became apparent, as the twinning hypothesis proposed by Donnay *et al.* in 1958 for digenite was found to apply also in the case of metastable bornite (Morimoto, in preparation).

The cubic edifice of the metastable form is inter-

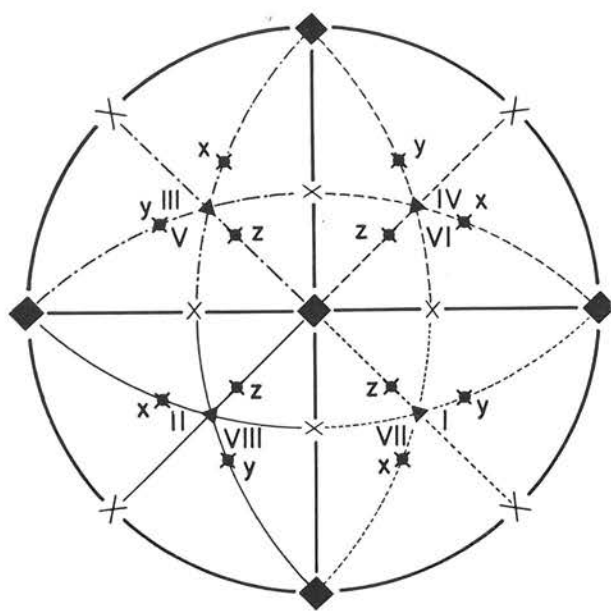


FIG. 1. Stereographic projection on  $(001)_c$  of the twin in metastable bornite.

preted as an aggregate of a large number of small domains in eight different orientations. All the domains that have the same orientation constitute *one crystal*, even if they are not singly connected. Each such crystal has rhombohedral symmetry with  $a_{rh} = 6.70 \text{ \AA}$  and  $\alpha = 33^\circ 32'$ , and the space group  $R3m$ . These eight crystals are in twin relations, shown in Fig. 1.

Figure 2 shows the structure of the rhombohedral metastable form. This structure can be derived from that of the cubic high-temperature form as follows. All the sulfur atoms remain in place, retaining the cubic close-packing. Of the four sulfur tetrahedra sites, two do not change at all. One becomes vacant, and the metal atom which occupied it in the high-temperature form is redistributed among the other three sites. The corresponding three sulfur tetrahedra now contain one full metal atom each. To compensate for the vacant site, the last metal site is moved slightly. The statistical distribution of  $\frac{3}{4}$  of a metal atom among twenty-four possible sites inside each sulfur tetrahedron changes to the statistical distribution of one metal atom among four possible sites.

#### LOW-TEMPERATURE FORM

Strong and medium reflections have similar intensity distribution in both the metastable and the low-temperature forms, indicating that the two structures have a common basic structure. The reflections

of the low-temperature form, however, do not obey the special extinction rule.

There are two different ways to explain the disappearance of the special extinction rule in the low-temperature form: (a) disappearance of the twinning or (b) lowering of the crystal symmetry (or symmetry of the domain orientation) from rhombohedral to monoclinic keeping the twin relation.

It is unlikely that the low-temperature form would have higher symmetry form. The structure of the low-temperature form, therefore, can be derived as twinning of domains with monoclinic symmetry.

#### THE TRANSITION

Figure 3 shows the structural relations among the three polymorphs, all of which are represented as layer structures parallel to  $(111)_{rh}$ . The structures of single crystals (= domain orientations) are shown for the metastable and low-temperature forms.

All three structures are built on the basis of the cubic close-packing of the sulfur atoms. The statistically distributed metal atoms are represented as bands in the high-temperature and metastable forms. The MI layers move closer to sulfur layers to compensate for the vacant layers in the metastable and low-temperature forms. The distance between the MI layer and the sulfur layer becomes shorter, which sug-

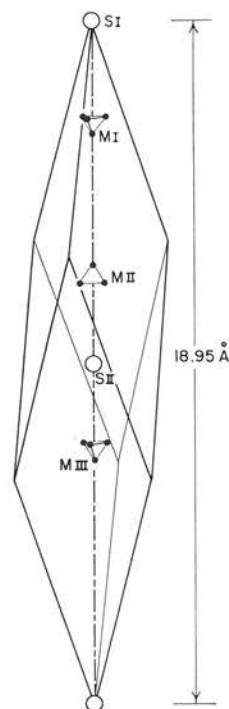


FIG. 2. The crystal structure of metastable bornite.

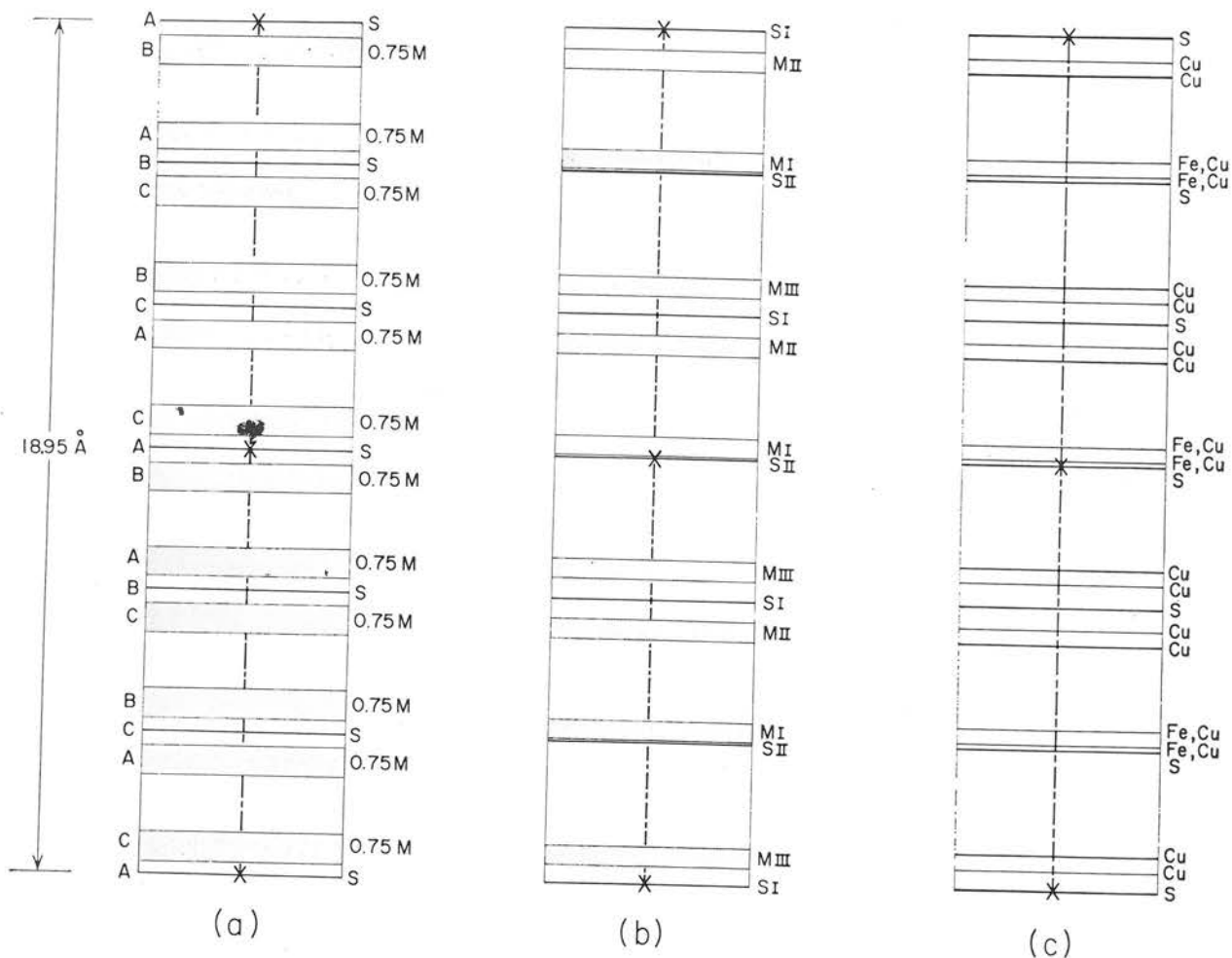


FIG. 3. Layer structures of three polymorphs of bornite: (a) high-temperature, (b) metastable, and (c) low-temperature form.

gests the possibility that the Fe atoms concentrate in the MI layers.

Although the structure of the low-temperature form was not actually determined, it seems likely that the metal atom, statistically distributed at the four corners of a tetrahedron in the metastable form, will occupy one of the four sites in the low-temperature form. Assuming the stoichiometric composition for the low-temperature bornite the Fe atoms must take some special positions, the MI tetrahedra, which give a distance of 2.20 Å from the sulfur atom. The other metal positions are more than 2.27 Å away from sulfur atoms and are supposedly occupied by Cu atoms. This relation in the low-temperature form is shown by lines in Fig. 3.

The arrangements of the metal vacant layers change their orientation according to a simple *twin law* in the metastable and low-temperature forms, as already mentioned. Domain structures always take

place on transition from the high-temperature to metastable or low-temperature forms, indicating that the vacant metal layers cannot stably keep their orientation over a long distance. The diffracted  $x$ -rays from each crystal (= domain orientation) are not coherent with those from other crystals. The domains themselves must be small since the twins cannot be recognized as such by direct methods of observation. The volumes of the different domain orientations must be nearly equal so as to give cubic or tetragonal symmetry for the specimen as a whole.

#### TWINNING DOMAIN STRUCTURE

Specimens of the metastable and low-temperature bornites can be described as twins in which the individual crystals are composed of a large number of small domains that need not be singly connected. They are different from usual twins, however, in that most of the atoms build a continuous periodic struc-

ture throughout the whole edifice, so that the twin relations apply only to the vacant metal positions. It follows that the prerequisite for twinning, namely the existence of a multiple cell with higher symmetry or pseudosymmetry, is here exactly satisfied, and

twinning should be frequent—as indeed it is; it always accompanies the transition. Such slight structural rearrangements take place that the heat of transition should be very small and the transition unquenchable.

## REFERENCES

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