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BORNITE (Cu_5FeS_4): STABILITY AND CRYSTAL STRUCTURE OF THE INTERMEDIATE FORM

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ABSTRACT

The intermediate form of bornite (Cu_5FeS_4) has been determined to be stable in the range from 170°C to 235°C by differential scanning calorimetry and high-temperature X-ray methods. The changes in the cell dimensions on rapid cooling indicate the appearance of a transitional metastable form after the high form, different from the intermediate form.

The crystal structure of the intermediate form has been determined at 185°C. The space group is *Fm3m*, and *a* 10.981(1)Å. Sulfur atoms form the ideal cubic closest packing, and metal atoms are distributed statistically in the tetrahedral interstices among sulfur atoms. The structure consists of two different kinds of cubes with the antifluorite-type structure; one has half a metal atom in each tetrahedron and represents disorder of Cu atoms and vacancies, whereas the other has one metal atom in each tetrahedron and represents disorder of Cu and Fe atoms. The intermediate form represents a stage between the low and high forms.

SOMMAIRE

Le champ de stabilité de la forme intermédiaire de bornite (Cu_5FeS_4) s'étend de 170° à 235°C, ainsi qu'on l'a déterminé par calorimétrie différentielle à balayage et par diffraction-X à haute température. Un refroidissement rapide de la forme de haute température modifie les dimensions de la maille, signalant ainsi l'apparition d'une forme de transition métastable, différente de la forme intermédiaire. La structure cristalline de la forme intermédiaire a été determinée à 185°C: groupe spatial *Fm3m, a* 10.981(1)Å. Les atomes de soufre constituent un empilement compact cubique, et les atomes métalliques occupent, de façon aléatoire, les trois quarts des interstices tétraédriques. La structure contient des mailles de deux sortes du type antifluorine, les tétraèdres étant occupés, dans les unes, à raison d'un demi-atome de cuivre par tétraèdre et, dans les autres, par un atome métallique. Dans les premières, le désordre se produit entre atomes de cuivre et lacunes; dans les secondes, ce sont les atomes Cu et Fe qui sont désordonnés. La forme intermédiaire représente un stade structural transitionnel entre les formes de haute et de basse température.

(Traduit par la Rédaction)

INTRODUCTION

In spite of extensive studies of natural and synthetic bornite (Cu_5FeS_4), the polymorphic relations and the crystal structures of the polymorphs remained unsolved. Frueh (1950) studied the polymorphic relations of bornite with X-ray, thermal and electrical methods and found two polymorphs: low- and high-temperature forms (hereafter low and high forms, respectively). Morimoto & Kullerud (1961) described two stable forms (low and high forms) and one transitional metastable form found through use of high-temperature single-crystal X-ray methods. They found the high form to be stable above 228°C, and to gradually change at room temperature to the low form through a transitional stage. However, DTA curves (Sugaki & Shima 1965), the magnetic susceptibility (Allais 1965) and electrical resistance and magnetic susceptibility of bornite (Takeno *et al.* 1968) indicated the existence of another stable intermediate-temperature form (hereafter intermediate form) between the low and high forms. However, the relations between the metastable and intermediate forms have not yet been clarified.

The structure of the high form was determined to be of antifluorite type with *a* 5.50Å and space group *Fm*3*m* (Morimoto 1964). The metal atoms are statistically distributed among 24 equivalent sites in the sulfur tetrahedron. The crystal structure of the metastable form was studied by Morimoto (1964) and Allais (1968). This form gives apparent cubic symmetry with space group *Fd*3*m* and a cell dimension of *a* 10.94Å, twice that of the high form. Reflections in the X-ray diffraction pattern show extra systematic absences in that only reflections with *h, k, l* all odd, all $4n$ or all $4n+2$ appear. Morimoto (1964) explained these extra systematic absences by a twin hypothesis based on a structure consisting of incoherent domains with

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rhombohedral symmetry, a structure first proposed by Donnay *et al.* (1958) for synthetic digenite. However, Allais (1968) considered the size of the rhombohedral domains to be of the order of coherency of the X-rays and determined a statistical structure of cubic symmetry. In both structures, sulfur atoms form the ideal cubic closest packing. The metal atoms are distributed statistically in the tetrahedral interstices in the sulfur-atom array.

A variety of cell dimensions and space groups has been reported for the low form (Tunell & Adams 1949, Frueh 1950, Morimoto & Kullerud 1961). Koto & Morimoto (1972, 1975) have shown that the low form is orthorhombic (pseudotetragonal) with a 10.950(1), b 21.862(2), c 10.950(1)Å, space group *Pbca*. If the high and the transitional forms are represented by $a \times a \times a$ and $2a \times 2a \times 2a$ cells, respectively, the low form is represented by a $2a \times 4a \times 2a$ supercell. Koto & Morimoto (1975) determined the structure of the low form by a modified partial Patterson function. As will be described later in more detail, the structure is characterized by a mosaic pattern arrangement of two structural units: antifluorite-type and sphalerite-type cubes.

Putnis & Grace (1976) have observed the phase transformations of bornite by transmission electron microscopy. They found that two types of $2a \times 2a \times 2a$ supercells are produced from the high form by different cooling rates. The $2a \times 2a \times 2a$ supercell with the systematically absent supercell reflections is obtained by rapid cooling; this corresponds to the metastable form. Slow cooling leads to another $2a \times 2a \times 2a$ supercell without systematic absences. This may correspond to the intermediate form described in this paper.

In this investigation, the stability range of the intermediate form of bornite has been determined by differential scanning calorimetry (DSC) and high-temperature X-ray single-crystal methods. The crystal structure of the intermediate form also has been determined and is compared with those of other polymorphs of bornite.

STABILITY RELATIONSHIPS

Materials

Bornite from Redruth, Cornwall, England and synthetic bornite (Cu_5FeS_4) were used for the thermal analysis and the high-temperature X-ray study. Bornite was obtained by dry synthesis from a starting mixture of copper, iron and sulfur in the ratio 5:1:4. The purity of the metals was 99.99% and that of the sulfur 99.999%.

The mixture was heated at 700°C for a day and was quenched in cold water. The reaction product was ground in acetone; heating and grinding were repeated two more times. After heating at 500°C for twenty days, the product was cooled very slowly. The final product was identified, by X-ray powder diffraction and reflection microscopy, as the low form of bornite.

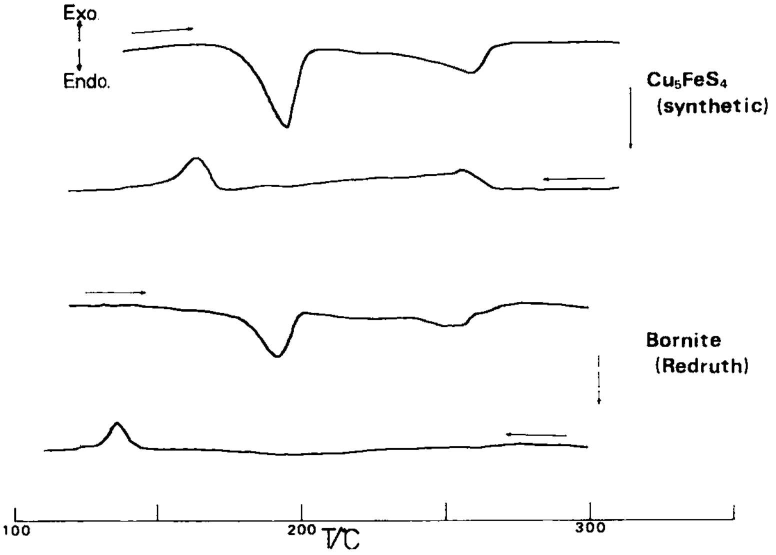

FIG. 1. DSC curves for synthetic bornite and bornite from Cornwall, England.

Thermal analysis by DSC

Thermal analysis of natural bornite and synthetic Cu_5FeS_4 was obtained with DSC. The DSC curves were measured from room temperature to 450°C and *vice versa* in nitrogen at one atmosphere pressure, using an aluminum sample holder. The rates of increase and decrease of temperature were 10 and 5°C/min., respectively. Temperature was measured by a Pt-Platinel thermocouple and controlled automatically.

The DSC curves of synthetic and natural bornite are shown in Figure 1. Two endothermic peaks appear as temperature is increased. One peak begins at about 170°C and is complete at 200°C for both synthetic and natural bornite. The other peak is broad and weak and extends over a range from 200°C to 260°C. The DSC curves are similar to the DTA curves reported by Sugaki & Shima (1965), though the peaks are shifted toward the higher temperature side by 5 to 10°C in the latter. On cooling, the DSC curve of synthetic bornite shows two exothermic peaks, whereas that of natural bornite shows only one peak displaced toward lower temperature. The DSC curves are reproducible on repeated runs, although the exothermic peak on the high-temperature side becomes insignificant for natural specimens on cooling.

TABLE 1. CELL CONSTANTS OF BORNITE AT ELEVATED TEMPERATURES

T(°C)	a(Å)	b(Å)	c(Å)	V(Å³)
24	10.958(2)	21.858(5)	10.951(2)	2623.0(9)
50	10.959(2)	21.879(3)	10.957(3)	2627.3(7)
75	10.964(2)	21.881(2)	10.965(1)	2630.7(5)
100	10.968(2)	21.895(2)	10.969(1)	2634.0(6)
125	10.972(2)	21.913(4)	10.973(2)	2638.2(9)
150	10.972(2)	21.917(3)	10.977(1)	2640.7(6)
165	10.983(1)	21.933(3)	10.979(1)	2644.6(6)
175	10.9766(7)			1322.5(2)
185	10.9806(8)			1324.0(3)
195	10.9835(6)			1325.0(2)
210	10.9890(4)			1327.0(2)
220	10.9912(6)			1327.8(2)
230	10.9952(4)			1329.3(1)
240	5.5075(2)			167.06(2)
260	5.5106(4)			167.34(4)
300	5.5166(6)			167.89(5)
250	5.5106(6)			167.34(6)
240	5.5106(4)			167.34(3)
230	5.5095(3)			167.24(2)
220	11.0134(8)			1335.9(3)
210	11.0096(9)			1334.5(3)
200	11.0026(5)			1331.9(2)
190	10.9962(6)			1329.6(2)
180	10.9915(8)			1327.9(3)
170	10.9882(4)			1326.7(1)
160	10.985(1)	21.928(2)	21.958(2)	
120	10.980(1)	21.904(2)	21.938(2)	
80	10.971(2)	21.882(2)	21.920(3)	
28	10.959(1)	21.862(2)	21.902(2)	

X-ray study

Natural bornite was used for a high-temperature single-crystal X-ray study. Precession and cone-axis photographs at room temperature, 195°C, and 265°C show diffraction patterns of the low, intermediate and high forms, respectively. The diffraction pattern of the low form shows orthorhombic symmetry as reported by Koto & Morimoto (1975). The intermediate form has weak reflections such as 200 and 600 that were not observed in the metastable form reported by Morimoto (1964) and Allais (1968). The lack of systematic absences in the intermediate form indicates that its possible space group is $Fm3m$, $F\bar{4}3m$ or $F432$.

A single crystal of 0.10×0.08×0.08 mm was used for determination of the cell dimensions at high temperatures. The crystal was enclosed in an evacuated silica capillary tube 0.1 mm thick, and was heated with a small furnace attached to a four-circle diffractometer. Temperature was measured by a thermocouple attached near the crystal and controlled within ~1°C. The 2θ values were measured from room temperature to 300°C at intervals of 10-20°C using Mo$K\alpha$ radiation (λ=0.70926Å). The specimen was kept for 30 minutes at constant temperature before measurement and about two hours were necessary to obtain the 2θ values of the necessary reflections at constant temperatures. The cell dimensions were determined by the least-squares refinement of from 5 to 13 independent reflections.

The cell dimensions of bornite are listed for different temperatures in Table 1. In Figure 2, the cell dimensions are shown as a function of temperature in terms of those of the respective subcells: $a/2$, $b/4$ and $c/2$ for the low form and $a/2$ for the intermediate form. Changes of the cell dimensions take place discontinuously at about 170°C and 235°C when temperature is increased. These changes correspond to the phase transitions from the low to intermediate form and from the intermediate to high form, respectively, as detected by the DSC curves for natural bornite (Fig. 1).

When temperature is decreased, however, the change of the cell dimension at the transition of 230°C is continuous and the lines representing the change of the cell dimensions show slightly different inclinations above and below the transition temperature. This continuous change of the cell dimension at the transition explains well the fact that the transition was not detected in the DSC cooling curve for natural bornite. The other phase transition takes place at about 165°C, which is lower by 5°C than in the case of heating. In this transition, the single crystal changed into twinned crystals of orthorhombic symmetry with a 10.959(1), b 21.862(2), c 21.902(2)Å at 28°C.

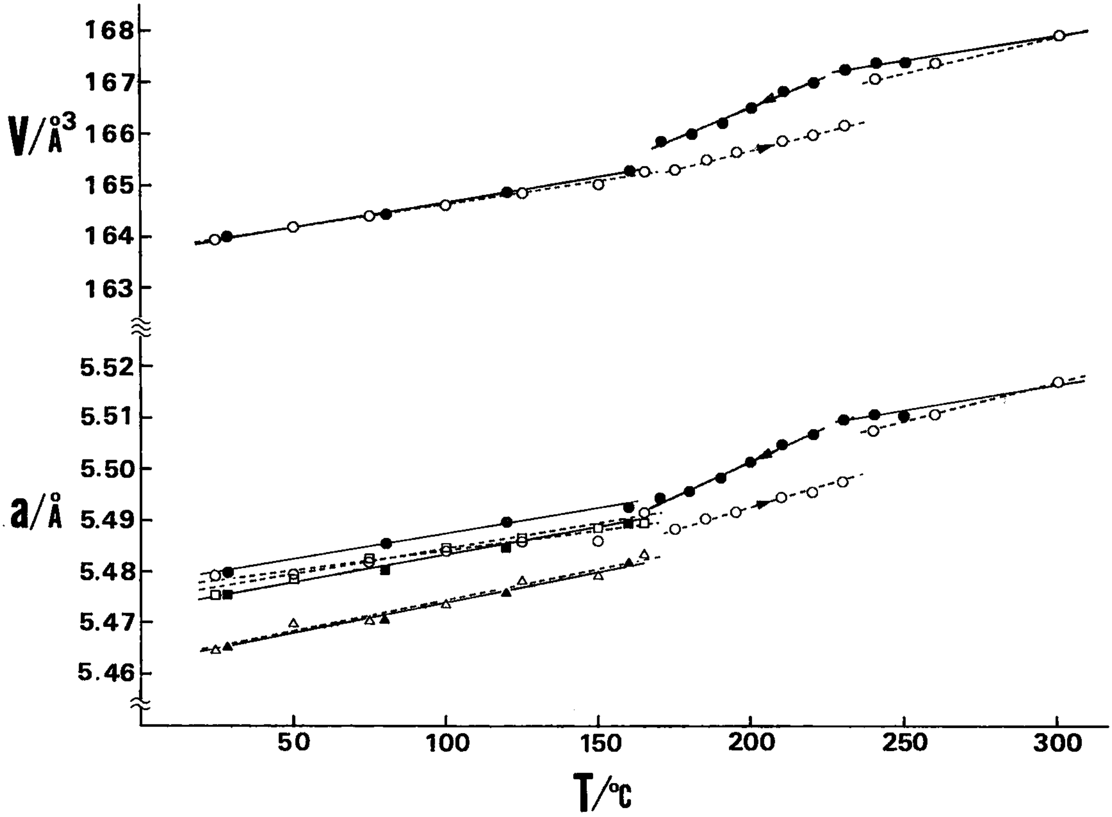

FIG. 2. Cell dimensions and volumes as a function of temperature for natural bornite for increasing temperature (dotted lines) and for decreasing temperature (solid lines). The cell dimensions and volumes of the subcells are plotted for the low and intermediate forms. Circles, triangles and quadrangles of the low form are *a, b* and *c* axes, respectively.

Discussion

The thermal analysis and high-temperature X-ray study have confirmed that bornite exists in three stable polymorphs: low, intermediate and high forms. The low form changes to the intermediate form at 170°C and the latter changes to the high form at 235°C. The change in cell dimensions as a function of temperature (Fig. 2) indicates the existence of a transitional state, because the cell dimensions observed at the same temperatures differ and depend on whether temperature is increasing or decreasing. When temperature increases, the change in the cell dimensions is discontinuous at the transition temperature from the intermediate to the high form, indicating a transition of the first order. However, when temperature decreases, a different kind of transition takes place at almost the same temperature, in which the cell dimension of a new phase is continuous with that of the high form. This transition is, therefore, apparently of a higher order. The cell dimensions of this new phase are closer to those of the high form than to the intermediate form. The metastable form, characterized by the rule for extra systematic absences in the diffraction patterns (Morimoto 1964; Allais 1968; Putnis & Grace 1976), is considered to be this new phase supercooled to room temperature from the high form.

A similar feature is observed in the low form inverted from the meastable form: the *c* axis of the low form maintains continuity with the cell dimension of the metastable form at the transition temperature. In this case, the low form is considered to maintain to some extent the disordered arrangement of atoms which does not exist in natural bornite.

CRYSTAL STRUCTURE OF THE INTERMEDIATE FORM

Intensity measurement

Intensity data were collected at 185°C with a four-circle diffractometer from the crystal used for the determination of the cell dimensions. Mo$K\alpha$ radiation monochromatized with pyrolytic graphite was used throughout this investigation. The furnace and the temperature-control system are the same as used for the measurement of the cell dimensions.

All reflections h, k and $l \geqslant 0$ were measured within the range $2\theta < 70°$. The intensities were corrected for Lorentz and polarization factors. The value of μR is 1.0 for the crystal and no absorption correction was made. The intensities of equivalent reflections agree well for most reflections, but they differ slightly for the weak supercell reflections. Therefore, the intensities of 187 independent reflections were obtained by averaging the intensities of equivalent reflections. Of 187 measured intensities, 171 with $|F_o| > 2\sigma(|F_o|)$ were regarded as 'observed reflections'.

Structure analysis

The cell dimension of the intermediate form at 185°C is 10.9806Å (Table 1). Possible space groups of the intermediate form are $Fm3m$, $F\bar{4}3m$ and $F432$, as determined from the diffraction aspect. The space group of the intermediate form was assumed to be centrosymmetric $Fm3m$, because only $Fm3m$ includes $Pbca$ of the low form as one of the subgroups.

The structures of the low and intermediate forms must be explained as superstructures of that of the high form. The differences among the structures of these three polymorphs are due mainly to the arrangement of metal atoms and vacancies in the tetrahedra of sulfur atoms which form the face-centred cubic arrangement. The structure of the intermediate form with the space group $Fm3m$ has two non-equivalent tetrahedra of sulfur atoms in an asymmetric unit. There are six metal atoms in the subcell with $a' \simeq 5.5$Å, and each sulfur tetrahedron on the average contains ¾ metal atoms. Therefore, two crystallographically different tetrahedra accommodate 3/2 metal atoms in all, no matter what the detailed distribution of the metal atoms is among the two tetrahedra.

The average structure of the low form based on the unit cell of the intermediate form (Koto & Morimoto 1975) indicates the existence of two kinds of tetrahedra, one occupied by half a metal atom and the other by one metal atom. Therefore, the structure model of the intermediate form was constructed on this distribution of metal atoms. Sulfur atoms were first kept at the nodes of a cubic face-centred lattice and metal atoms at the centres of the tetrahedra.

TABLE 2. FINAL ATOMIC PARAMETERS AND WEIGHTS FOR THE INTERMEDIATE FORM OF BORNITE AT 185°C

Atom	Wyckoff notation	x	y	z	B(Å^2)	ω
M(1-1)	32f	0.0909(10)	x	x	4.6(3)	0.31(4)
M(1-2)	96k	0.1295(16)	x	0.1069(23)	1.6(4)	0.07(1)
M(2)	96k	0.3614(5)	$1/2-x$	0.1133(8)	3.5(2)	0.33(1)
S(1)	24e	0.2535(7)	0	0	2.4(1)	
S(2)	8c	1/4	1/4	1/4	2.6(2)	

Starting from this model, the coordinates and weights of metal atoms and the isotropic temperature factors were refined by the full-matrix least-squares program of the UNICS system (Sakurai 1967). The scattering factor of the metal atom is assumed to be $(5f_{Cu}+f_{Fe})/6$. The R value obtained in this refinement was 0.27 for the observed reflections.

The metal atoms kept their initial weights but were displaced from the centres of the tetrahedra, and acquired large temperature factors. At this stage of the analysis, a difference Fourier synthesis showed four positive peaks around each metal atom, which were displaced towards the faces of the sulfur tetrahedra. The metal atoms were then divided into four sites and successive difference Fourier syntheses were done.

In the final structure, the $M(1)$ atom was divided into four sites displaced from the cen-

TABLE 3. OBSERVED AND CALCULATED STRUCTURAL FACTORS FOR INTERMEDIATE BORNITE

k	l	F_o	F_c
h = 0			
0	2	45.5	59.9
0	4	603.1	566.5
0	6	35.8	55.6
0	8	526.4	528.9
0	10	4.9	5.1
0	12	15.5	14.4
0	14	6.4	24.4
0	16	59.1	63.9
2	2	30.9	33.6
2	4	4.6	17.5
2	6	39.8	41.5
2	8	17.2	17.7
2	10	8.8	8.4
2	12	6.7	13.6
2	14	4.7	3.1
2	16	3.3	2.1
4	4	884.4	921.3
4	6	5.7	11.3
4	8	106.9	108.9
4	10	2.9	19.6
4	12	181.2	169.3
4	14	9.7	15.9
4	16	7.4	22.6
6	6	42.5	50.8
6	8	14.2	34.4
6	10	11.9	8.9
6	12	13.6	20.1
6	14	11.5	9.4
6	16	4.0	4.3
8	8	282.3	259.3
8	10	11.4	20.2
8	12	15.9	10.7
8	14	7.1	11.0
10	10	9.1	6.4
10	12	10.4	11.5
10	14	4.1	8.8
12	12	98.8	60.4
h = 1			
1	1	36.9	48.6
1	3	211.7	180.9
1	5	46.6	37.5
1	7	147.5	158.6
1	9	18.6	1.4
1	11	77.6	74.3
1	13	15.4	8.6
1	15	9.0	9.2
1	17	7.2	1.1
3	3	195.8	188.5
3	5	73.3	88.0
3	7	116.5	130.7
3	9	7.4	13.6
3	11	36.2	36.8
3	13	4.7	2.9
3	15	8.5	14.9
3	17	3.6	6.8
5	5	33.0	43.7
5	7	102.7	104.7
5	9	7.3	33.3
5	11	59.8	44.1
5	13	19.1	2.1
5	15	7.8	11.1
7	7	33.3	37.2
7	9	24.7	27.5
7	11	17.4	22.5
7	13	7.6	5.3
7	15	3.8	0.3
9	9	6.8	6.1
9	11	20.0	12.4
9	13	19.0	14.4
9	15	0.0	0.8
11	11	20.2	2.0
11	13	12.7	1.4
h = 2			
2	2	394.2	357.4
2	4	0.0	15.7
2	6	280.4	254.5
2	8	6.6	6.1
2	10	119.9	121.4
2	12	0.0	2.2
2	14	63.8	68.2
2	16	9.5	3.2
4	4	4.0	1.7
4	6	11.3	16.9
4	8	12.2	13.3
4	10	6.6	3.2
4	12	0.0	6.7
4	14	0.0	4.0
4	16	11.7	1.6
6	6	107.5	129.2
6	8	16.4	5.6
6	10	129.8	123.8
6	12	8.2	9.7
6	14	39.1	47.6
6	16	14.1	0.8
8	8	11.6	3.1
8	10	6.9	6.3
8	12	7.1	0.4
8	14	7.2	1.5
10	10	56.7	54.8
10	12	11.4	2.6
10	14	22.6	37.1
12	12	18.4	2.4
h = 3			
3	3	211.2	204.8
3	5	113.8	112.7
3	7	90.7	93.0
3	9	48.0	37.2
3	11	53.4	48.4
3	13	7.1	0.9
3	15	15.8	2.8
3	17	0.0	0.0
5	5	0.0	20.1
5	7	75.2	73.4
5	9	9.3	5.3
5	11	49.7	36.5
5	13	0.0	14.0
5	15	14.5	3.8
5	17	0.0	2.2
7	7	78.5	70.0
7	9	35.2	28.9
7	11	12.7	11.7
7	13	13.4	5.9
7	15	12.3	11.3
9	9	7.0	18.8
9	11	9.3	11.2
9	13	7.4	4.7
9	15	0.0	4.7
11	11	18.7	15.9
11	13	7.8	3.2
h = 4			
4	4	240.1	270.3
4	6	5.6	10.6
4	8	349.6	365.2
4	10	5.8	17.3
4	12	0.0	12.0
4	14	0.0	16.5
4	16	55.6	52.4
6	6	27.8	21.3
6	8	6.8	22.2
6	10	3.1	1.7
6	12	17.4	13.1
6	14	12.1	7.3
6	16	3.5	0.8
8	8	20.1	16.0
8	10	11.1	17.7
8	12	118.7	101.0
8	14	6.4	5.7
10	10	0.0	7.3
10	12	4.2	5.0
10	14	9.8	8.5
12	12	0.0	12.9
h = 5			
5	5	66.9	80.0
5	7	48.2	62.7
5	9	25.2	12.3
5	11	18.4	29.6
5	13	6.7	13.0
5	15	17.8	3.1
7	7	49.6	37.4
7	9	6.2	3.7
7	11	12.2	5.0
7	13	8.6	5.4
7	15	8.2	6.7
9	9	16.8	23.2
9	11	0.0	4.2
9	13	4.3	0.5
11	11	6.6	7.1
h = 6			
6	6	218.1	197.9
6	8	5.6	15.5
6	10	16.4	49.0
6	12	8.1	11.6
6	14	48.0	51.7
8	8	13.3	8.6
8	10	6.5	9.2
8	12	4.7	1.0
8	14	7.2	6.1
10	10	78.6	74.0
10	12	7.0	8.9
h = 7			
7	7	38.3	31.1
7	9	22.4	15.9
7	11	26.3	28.1
7	13	8.7	7.9
9	9	0.0	2.8
9	11	25.6	10.9
9	13	8.0	11.0
h = 8			
8	8	140.5	136.4
8	10	7.4	4.5
8	12	8.3	15.6
10	10	7.6	9.8
10	12	13.0	0.4
h = 9			
9	9	25.0	0.1
9	11	8.0	5.8

tre towards the faces of the tetrahedron, whereas the *M*(2) atom was divided into only three sites slightly displaced around a three-fold axis. The coordinates and weights of all atoms were finally obtained by full-matrix least-squares refinement. Although the total number of metal atoms was not constrained in this refinement, the total number converged to 48.3 per unit cell. The *R* value is 0.175 for all reflections and 0.165 for observed reflections. The final atomic parameters are given in Table 2, and the comparison of $|F_o|$ and $|F_c|$ in Table 3. All computations were done at the Computation Centre of Osaka University.

Description of the structure

The projection along the *a* axis is shown schematically in Figure 3. Sulfur atoms form the cubic closest packing and metal atoms are statistically distributed in the sulfur tetrahedra. The structure is characterized by a three-dimensional alternating arrangement of two kinds of cubes denoted by *M*1 and *M*2 (Fig. 4). Both cubes have the unit-cell dimensions of the high form and have the antifluorite-type structure, though they contain different numbers of metal atoms.

In the *M*1 cubes, each sulfur tetrahedron contains one *M*(1–1) and three equivalent *M*(1–2) atoms (Fig. 4). The total number of metal atoms is 0.52 in each tetrahedron. Therefore, each *M*1 cube with eight tetrahedra contains approximately four metal atoms. On the other hand, each tetrahedron in the *M*2 cube contains three equivalent *M*(2) atoms (Fig. 4). The total number of metal atoms in each tetrahedron is 0.99; therefore, each *M*2 cube contains about 8 metal atoms in all. The metal-sulfur distances are given in Table 4.

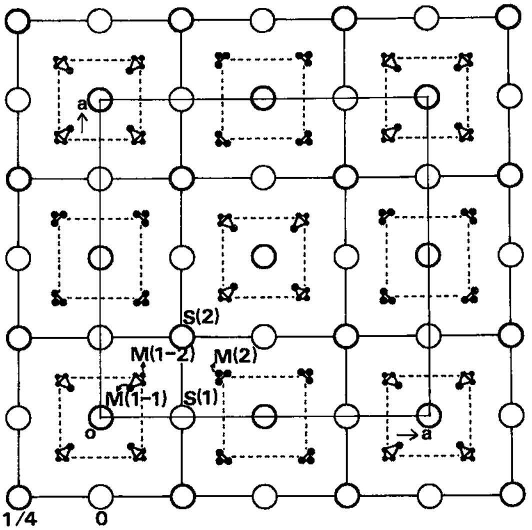

FIG. 3. The structure (from $z=0$ to ¼ of the unit cell) of the intermediate form. The *M*1 and *M*2 cubes are shown. Sulfur atoms are represented by large circles. Dotted lines join the centres of sulfur tetrahedra in the cubes.

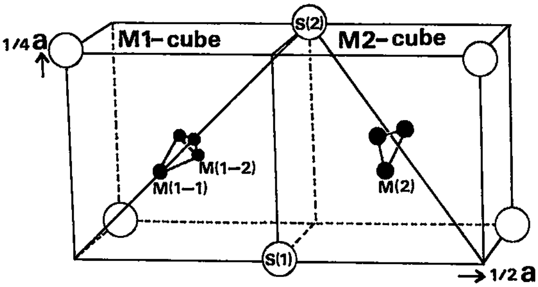

FIG. 4. The distribution of metal atoms in the sulfur tetrahedra in the intermediate form.

All the metal atoms are displaced towards the centres of the triangles of the sulfur tetrahedra. The *M*(1–1) and three *M*(1–2) atoms in the *M*1 cube are displaced from the centre of the tetrahedra toward the centres of the sulfur triangles forming the tetrahedra. The value of 2.28Å of the *M*(1–1)–S distances is equal to the value of 2.28Å found in a triangular coordination in the low form (Koto & Morimoto 1975). The average value of the three short *M*(1–2)–S distances is 2.34Å.

Triangular coordination of Cu atoms has been reported in several sulfide minerals (Evans & Konnert 1967), whereas Fe atoms have regular tetrahedral coordination in sulfide minerals. Therefore, the *M*1 cube is considered to be occupied only by copper atoms.

In the *M*2 cube, three *M*(2) atoms in a sulfur tetrahedron are slightly displaced from the centre of the tetrahedron towards the sulfur triangles around the three-fold axis. The average of 2.37Å for the *M*(2)–S distances is close to the average of 2.36Å for the metal-sulfur distances in the distorted tetrahedral coordination in the low form.

TABLE 4. METAL-SULFUR DISTANCES(Å) IN THE SULFUR TETRAHEDRON

	S(1)	S(2)	MEAN
M(1-1)	2.28(1) x3	3.03(1)	2.46 (2.28)
M(1-2)	2.29(2) x2 2.58(2)	2.44(2)	2.40
M(2)	2.30(1) x2 2.60(1)	2.29(1)	2.37

*The distance in the parenthesis is the mean of shortest three ones.

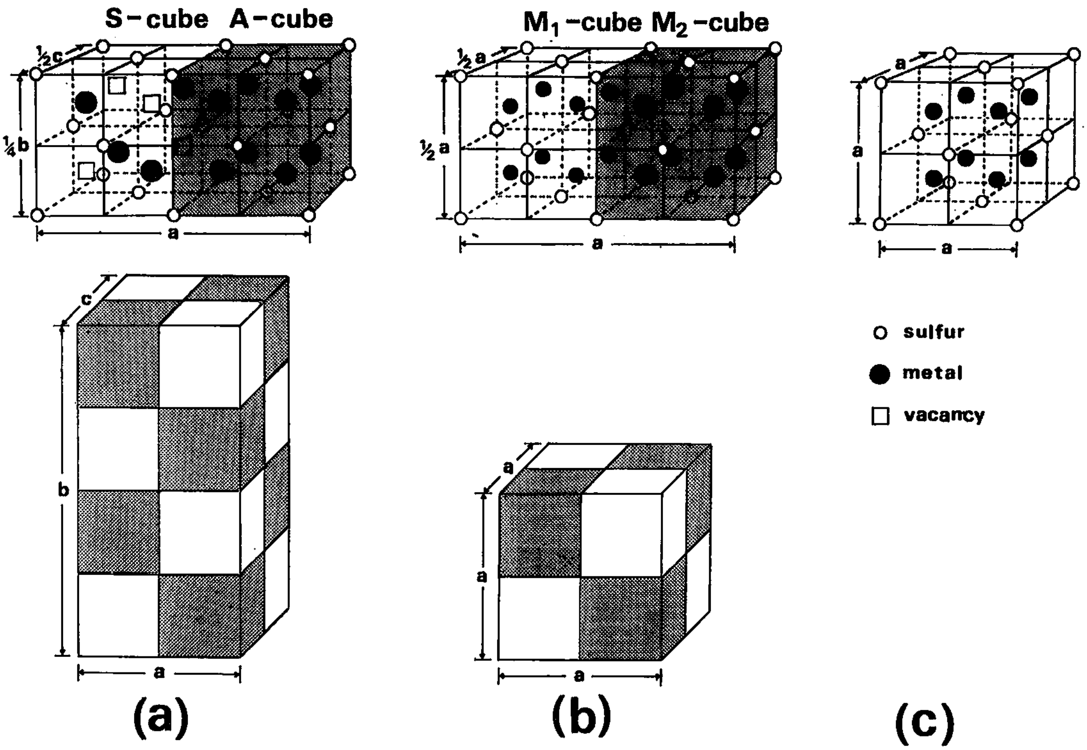

FIG. 5. Three polymorphs of bornite: (a) low form, (b) intermediate form and (c) high form. The statistical distributions of metal atoms in the sulfur tetrahedra are shown by solid circles representing the weights.

The large temperature factors of the metal atoms are considered to be due to positional disorder rather than to thermal vibrations at high temperature, because large temperature factors are obtained even for the metal atoms of the low form (Koto & Morimoto 1975). Splitting into three or four sites of metal atoms, as found in this investigation, approximates the actual statistical distribution of atoms as is discussed in more detail farther below.

Comparison of the structures of polymorphs

The structures of three polymorphs of bornite (low, intermediate and high forms) are schematically illustrated in Figure 5. The structure of the intermediate form is constructed from two different kinds of cubes as in the low form (Fig. 5b). These have the same size as the unit cell of the high form and alternate three-dimensionally, resulting in a mosaic arrangement. Both kinds of cubes of the intermediate form have the antifluorite-type structure, but those of the low form are of sphalerite-type (S) and antifluorite-type (A) (Fig. 5a).

From a structural viewpoint, the structure of the intermediate form can be considered to represent an intermediate stage between high and low forms. For example, the $M1$ and $M2$ cubes of the intermediate form contain numbers of metal atoms similar to the S and A cubes of the low form, respectively. Both $M2$ and A cubes have eight atoms that are slightly displaced towards the adjacent cubes. On the other hand, characteristic statistical distributions of the metal atoms are observed in both intermediate and high forms.

The statistical distribution of the intermediate form represents approximately the superposition of the atomic distribution of the low form displaced by $b/2$. Similarly, the statistical distribution of the high form represents the superposition of the intermediate forms displaced by $a/2$. The intermediate form can be interpreted as a partly disordered low form, because the intermediate form has long-range ordering in alternation of the S and A cubes, but has only short-range ordering in orientation of the S cubes of the low form. Disorder in orientation of the S cubes is possible by antiphase-domain boundaries with displacement vectors of $b/2$ or $(a+c)/2$ of the low form. Thus the intermediate form is considered to be an assemblage of the antiphase domains of the *S* and *A* cubes in the order of coherency for the X-rays. On the other hand, the intermediate form can be distinguished from the high form by long-range ordering of the *M*1 and *M*2 cubes and convergence of the statistical distribution of metal atoms to three or four positions from twenty-four possible positions in the sulfur tetrahedron.

Allais (1968) studied at room temperature the structure of bornite rapidly cooled from high temperature. This structure bears a close resemblance to the low form in that it forms sphalerite-like and antifluorite-like cubes. Based on this statistical structure, it is difficult to explain the observed extra systematic absences if cubic symmetry is assumed.

The metastable form seems to be closer to the high form than to the intermediate form judging from the cell-dimensions and the lack of extra systematic absences in the intermediate form. The experiment by Putnis & Grace (1976) also supports this. In the structure of the metastable form, some of the metal atoms retain the distribution of the high form, which must explain the extra systematic absences.

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