

Superstructure Investigation of Bornite, Cu_5FeS_4 , by the Modified Partial Patterson Function

BY KICHIRO KOTO AND NOBUO MORIMOTO

Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

(Received 5 November 1974; accepted 17 January 1975)

Bornite is orthorhombic with cell dimensions $a=10.950$ (1), $b=21.862$ (2) and $c=10.950$ (1) Å and space group $Pbca$. The modified partial Patterson function which is the self-convolution of the difference between the superstructure and hypothetical basic structure has been introduced and the ordered arrangement of metal atoms has been determined with this function. The R values are 0.101 for the substructure reflexions and 0.148 for 1008 observed superstructure reflexions. In the structure of bornite, sulphur atoms are arranged in cubic closest packing. Ordering of metal atoms in the tetrahedral or triangular interstices of sulphur atoms results in two structural units, antiferrotype and sphalerite-type cubes. Vacancies for metal atoms cluster in the sphalerite-type cube. The two different cubes alternate three-dimensionally and build the whole structure, resulting in a characteristic mosaic pattern structure.

Introduction

Three polymorphs of bornite Cu_5FeS_4 were described by Morimoto & Kullerud (1961): high, transitional and low forms. The high form is stable above 228°C and has cubic symmetry with $a=5.50$ Å and space group $Fm\bar{3}m$. The crystal structure was determined to be an antiferrotype (Morimoto, 1964). The high form changes to the transitional form on cooling below 228°C. It has an apparent cubic symmetry with space group $Fd\bar{3}m$ and cell dimension $a=10.94$ Å, twice that of the high form. The crystal structure was first studied by Morimoto (1964) and later by Allais (1968). In their structures, sulphur atoms are arranged in the ideal cubic closest packing and metal atoms are distributed statistically in the tetrahedral interstices of sulphur atoms in different ways.

The structure of the low form of bornite was studied by Lundqvist & Westgren (1936) and Tunell & Adams (1949) assuming cubic symmetry. Frueh (1950) considered that the structural difference between the low and high forms is one of order-disorder. Morimoto & Kullerud (1961) described a tetragonal cell with $a=10.94$ and $c=21.88$ Å and space group $P\bar{4}_2c$. They explained the various symmetries and cell dimensions for bornite reported in the literature as resulting from twinning of the tetragonal cell. However, all attempts to solve the structure based on this knowledge have been unsuccessful.

In this investigation, the true symmetry of bornite has been found to be not tetragonal but orthorhombic.

Since their introduction by Frueh (1953) and Buerger (1956), the partial Patterson functions which are calculated with superstructure reflexions alone have been successfully used for the investigation of superstructures. Sakurai (1958) also indicated the usefulness of the P_o function in structure analysis. The partial Patterson method derives a superstructure by determining the deviation from a substructure or an

average structure (Marumo, 1967). Takéuchi (1972) investigated the characteristics of the geometrical features of partial Patterson functions. The structure of bornite, however, could not be solved by this method. Modified partial Patterson functions, the principle of which was briefly described before (Koto & Morimoto, 1972), were introduced and the superstructure of bornite has been determined with this function.

Experimental

A few specimens of bornite with very small amounts of twin component were obtained by examining many crystals from Cornwall, England. Precession photographs of $h0l$ and $hk0$ layers taken with Ni-filtered $\text{Cu } K\alpha$ radiation from a high-power X-ray generator (30 kV, 60 mA) clearly indicated orthorhombic symmetry. The space group was determined uniquely on the basis of the systematic absences. No extra extinction rules were observed. Cell dimensions were determined by the least-squares refinement of 2θ values measured on back-reflexion Weissenberg films taken with $\text{Co } K\alpha_1$ radiation (1.78892 Å). Silicon was used as internal standard.

Bornite has a supercell of $2 \times 4 \times 2$ times that of the high form.

Crystal data

Orthorhombic (pseudotetragonal). Space group: $Pbca$, $a=10.950$ (1), $b=21.862$ (2), $c=10.950$ (1) Å. Cell content: $16\text{Cu}_5\text{FeS}_4$.

The intensity data were collected by a Rigaku four-circle diffractometer using Zr-filtered $\text{Mo } K\alpha$ radiation with the ω - 2θ scan technique. The specimen of $0.01 \times 0.01 \times 0.005$ cm was used for collecting the superstructure reflexions. Out of 2371 independent reflexions including 54 substructure reflexions within the range $(\sin \theta)/\lambda=0.60$, 1060 had intensities of greater than twice the standard deviations, based on

counting statistics, and were regarded as 'observed'. The change in intensity of the reflexions due to twinning was neglected because the amount of the twin component is very small. Intensities of the 54 independent substructure reflexions corresponding to the cell of $a \sim 5.5 \text{ \AA}$ with a face-centred lattice were measured using a small crystal $0.003 \times 0.003 \times 0.005 \text{ cm}$ and were used for the structure determination together with those of the superstructure reflexions. The data were then reduced in the usual way but without absorption or extinction corrections.

Modified partial Patterson functions

Suppose that superstructures can be described by changing electron density,* *i.e.*, order-disorder and replacement of atoms, and/or position of atoms, *i.e.* distortion from ideal structure, in a basic structure. Let electron density in a superstructure be $\rho_s(xyz)$ and that in a basic structure, $\rho_b(xyz)$. The difference between both structures is $\rho_d(xyz) = \rho_b(xyz) - \rho_s(xyz)$, where s , b and d represent superstructure, basic structure and difference structure. Let the Fourier transforms of $\rho_s(xyz)$ and $\rho_b(xyz)$ be $F_s(hkl)$ and $F_b(hkl)$, respectively. The Fourier transform of the difference structure is, therefore, $F_d(hkl) = F_b(hkl) - F_s(hkl)$. The Patterson function or the self-convolution of the difference structure is calculated with coefficients of $|F_d(hkl)|^2$. Generally we use a substructure or an average structure as a basic structure. Because a substructure is obtained with reflexions such as $h = PH$, $k = QK$ and

$l = RL$ where P , Q and R are constant integers and H , K and L are integers, $F_b(hkl)$ is different from zero only when h , k and l are PH , QK and RL , respectively. Therefore $F_d(hkl)$ is equal to zero for substructure reflexions. We calculate the Patterson function of the difference between the superstructure and substructure with superstructure reflexions alone, which is called a partial Patterson function. If the magnitude of displacement of atoms is small, partial Patterson functions are useful for the superstructure investigation. However, if the magnitude is large, a difficulty arises in the interpretation of the partial Patterson functions because of the obscuring of electron density in the substructure owing to superposition of atoms.

Instead of the substructure, we introduce another basic structure in which the electron density is as sharp as ordinary atoms and atoms are at ideal sites. For the calculation of the Patterson function of the difference structure, we have to take into account the difference between both sets of structure factors for all reflexions. However, if a basic structure has the same cell dimensions as the substructure, only the phases of the substructure reflexions need to be known. The phases of the substructure reflexions and the absolute intensity can be obtained by substructure determination. Patterson functions thus calculated are called modified partial Patterson functions. These are illustrated for two typically different cases. One is for a superstructure due to order-disorder, the other for one due to a distorted structure.

In the former case, let us consider an example of a one-dimensional superstructure due to an ordered arrangement of two different kinds of A and B atoms, where $f_A > f_B$ (Fig. 1). As a basic structure, we assume a substructure in which hypothetical atoms whose scattering factor is the mean of those for A and B atoms, are at ideal sites. We also assume another basic structure which consists of only A atoms at the ideal sites. In the case of a substructure, negative and positive peaks are found around A and B sites, respectively, in the difference structure. Therefore positive and negative peaks are found in the self-convolution of the difference structure. However, in the other case we find positive peaks around the B site and nothing around the A site. Therefore only positive peaks are found in the self-convolution of the difference structure. In the example of chalcopyrite CuFeS_2 (Frueh, 1953), a basic structure in which all metal sites are occupied by Cu or Fe atoms can be assumed instead of the average structure. Vacancies of atoms are considered as an extreme case of order-disorder (Marumo, 1967) and the self-convolution of the difference for vacancies results in positive peaks.

In the latter case, let us consider a superstructure due to a deviation of a constituent A atom from the ideal site (Fig. 2). If we assume a substructure as a basic structure, the positive and negative peaks in the difference structure are asymmetrical around ideal sites of displaced atoms and the residual peaks are also

* Takéuchi (1972) classified superstructures into three categories. However, the third category of superstructure involving the addition of atoms is considered to belong to this.

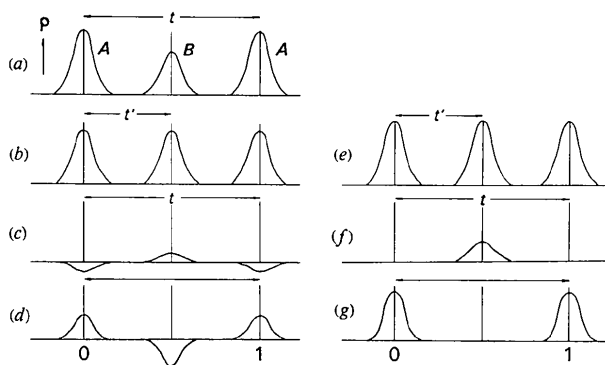


Fig. 1. (a) Illustration of a one-dimensional superstructure due to order-disorder. (b) The substructure or the average structure. (c) The difference between substructure and superstructure (the difference structure). (d) The self-convolution of the difference structure. (e), (f) and (g) correspond to Fig. 1(a) of Takéuchi (1972). (e) A basic structure in which every ideal site is occupied by an A atom. (f) The difference structure and (g) its self-convolution. Translation units t and t' are for the superstructure and basic structure, respectively, and ρ is the electron density. These have the same meaning in Figs. 2 and 3.

found around the atoms at ideal sites in the superstructure because of superposition of atoms in the substructure. If the magnitude of displacement is small, partial Patterson functions are useful and a good example has been shown by Takéuchi & Horiuchi (1972). If we assume another basic structure in which all constituent A atoms are at the ideal sites, the difference structure has the same features as the difference synthesis. The positive and negative peaks are symmetrical around ideal sites and therefore, in the self-convolution of the difference, the geometrical features reported by Takéuchi (1972) can be expected.

Both cases mentioned above generally occur together in a superstructure. The self-convolution of the difference structure results in a pair of positive and negative peaks which are symmetrical around the corresponding vectors (Fig. 3).

Application to the bornite structure

A modified partial Patterson method has been applied for the determination of the ordering of metal atoms in the structure of bornite with the following procedure.

From consideration of the cell dimensions, the structure consists of a cubic close packed framework of sulphur atoms and 128 tetrahedra of sulphur atoms are found in the unit cell. If each metal atom is considered to belong to a sulphur tetrahedron, 32 tetrahedra must remain vacant. First the substructure was determined with reflexions such as $h=2H$, $k=4K$ and $l=2L$ where H , K and L are all even or odd, assuming space group $Fm\bar{3}m$ of the antifluorite structure. In the substructure, metal atoms are distributed statistically in the tetrahedral interstices of sulphur atoms. Then we introduced a basic structure of an antifluorite-type having the same cell dimensions as the substructure and in which sulphur atoms occupy the nodes of the face-centred lattice and every centre of the sulphur tetra-

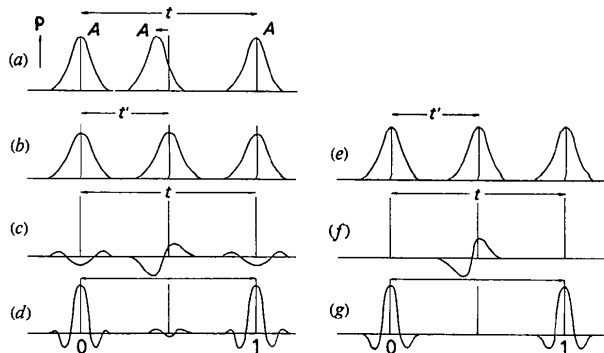


Fig. 2. (a) Illustration of a one-dimensional superstructure due to distortion. (b) The substructure. (c) The difference structure and (d) its self-convolution. Figs. (a), (b) and (c) correspond to Fig. 1(b) of Takéuchi (1972). (e) A basic structure in which every ideal site is occupied by an A atom. (f) The difference structure and (g) its self-convolution.

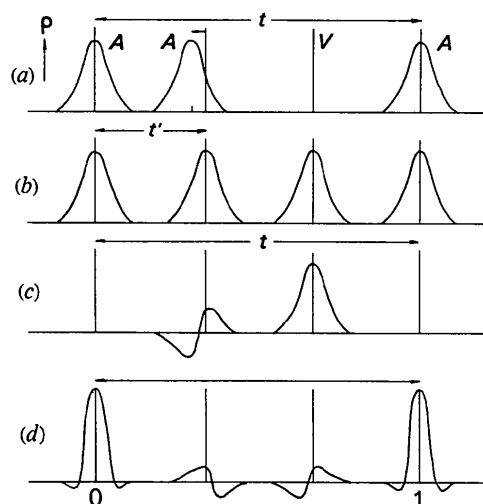


Fig. 3. (a) Illustration of a one-dimensional superstructure due to both order-disorder and distortion. Vacancy (V) for an atom is illustrated as a typical case of order-disorder. (b) A basic structure in which every ideal site is occupied by an A atom. (c) The difference structure and (d) its self-convolution.

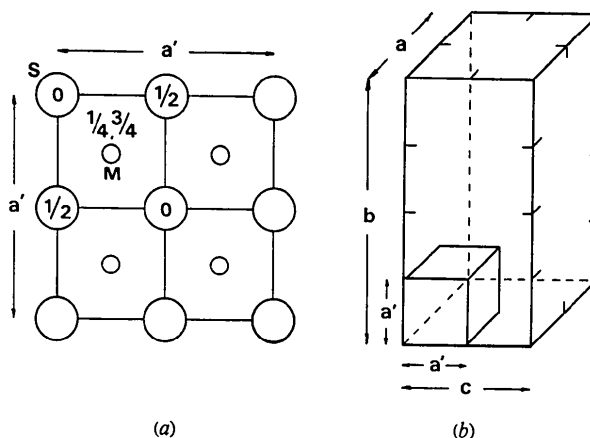


Fig. 4. (a) A basic structure of bornite with small cell dimensions of $a' \sim 5.5 \text{ \AA}$. M and S represent $(5\text{Cu} + \text{Fe})/6$ and sulphur atoms, respectively. The relationship between a basic cell and a supercell is shown in (b).

hedra is occupied by one metal atom with a weighted scattering factor of $(5f_{\text{Cu}} + f_{\text{Fe}})/6$ (Fig. 4). Isotropic temperature factors were assumed to be 0.5 \AA^2 for both metal and sulphur atoms.

The modified partial Patterson function was calculated with the coefficients of $|F_b(hkl) - F_s(hkl)|^2$ for substructure reflexions and $|F_s(hkl)|^2$ for superstructure reflexions. The signs of the substructure reflexions and an absolute scale factor were obtained by the substructure determination. In the modified partial Patterson maps, the vectors between vacancies for metal atoms are exaggerated in comparison with the ordinary partial Patterson maps (Fig. 5). By a minimum function method, taking into account only positive peaks in the modified ones, an ordered arrangement of vacancies was determined (Fig. 6).

Determination of distortion

The displacements of metal and sulphur atoms from the ideal positions were determined by successive Fourier and difference syntheses. The R value was 0.44

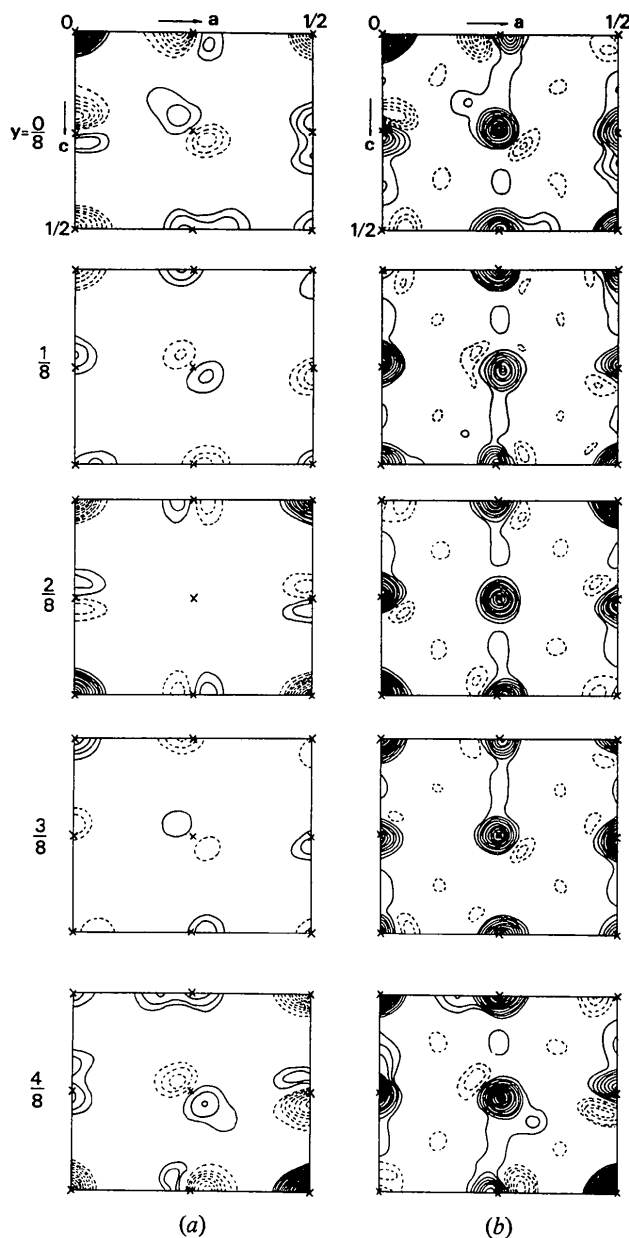


Fig. 5. Sections of an ordinary partial Patterson function (a) and a modified partial Patterson function (b) of bornite. Levels are indicated on the left-hand side. Contours are drawn at arbitrary intervals but on the same scale in both. Negative contours are shown as broken lines. Crosses represent the vectors between tetrahedral sites for metal atoms. The intense peaks around crosses in the modified partial Patterson sections are vectors between vacancies for metal atoms. Positive and negative peaks symmetrical around crosses indicate the distortion from the basic structure [cf. Fig. 3(d)].

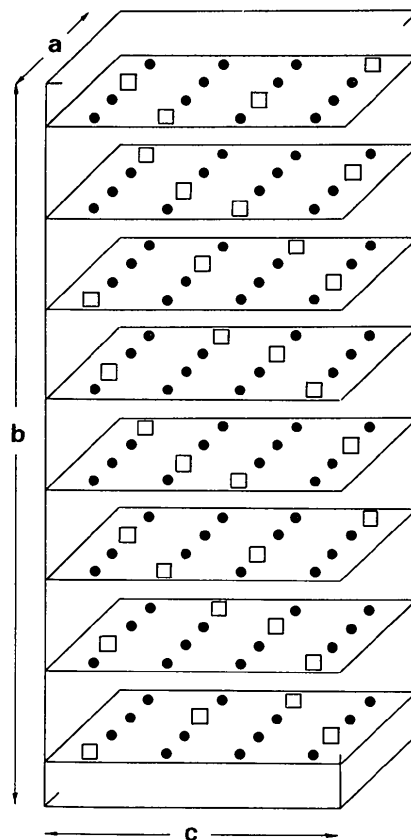


Fig. 6. Ordered arrangement of vacant tetrahedra of sulphur atoms in the bornite structure. Squares and small black circles represent the centres of the vacant tetrahedra of sulphur atoms and those of tetrahedra, each of which contains a metal atom, respectively.

for all reflexions at this stage. Subsequent block-diagonal least-squares refinements varying positional parameters and individual isotropic temperature factors, reduced the R values to 0.101, 0.216 and 0.345 for 54 substructure, 1008 observed superstructure and all 2371 reflexions, respectively. The standard error associated with the position of the metal atoms is $\sim 0.006 \text{ \AA}$ and of the sulphur atoms, $\sim 0.008 \text{ \AA}$. Isotropic temperature factors vary from 1.79 to 3.99 for the metal atoms and from 0.74 to 1.30 for the sulphur atoms. The weighted scattering factor of $(5f_{\text{Cu}} + f_{\text{Fe}})/6$ for metal atoms was used for the calculation of the structure factors. Scattering factors for non-ionized atoms were taken from *International Tables for X-ray Crystallography* (1962). An attempted absorption correction was unsuccessful and led to only larger errors in the coordinates. Further refinement with superstructure reflexions alone, the scale factor being kept constant, and gave rise to lower R values and better positional errors. The R values are 0.148 and 0.270 for 1008 observed and all 2317 superstructure reflexions, respectively. The positional standard errors are

~ 0.004 and ~ 0.006 Å for the metal and sulphur atoms, respectively. The fractional coordinates of the atoms, which are all in general positions, are given in Table 1. The anisotropic temperature factors are considered to have no physical meaning at this stage. Interatomic distances between metal and sulphur atoms are given in Table 2.*

Table 1. Atomic coordinates of bornite

M represents $(5\text{Cu} + \text{Fe})/6$. Standard deviations are given in parentheses in units of the last digit. Isotropic temperature factors are given.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
S(1)	0.0046 (5)	-0.0006 (2)	0.2541 (5)	0.74 (12)
S(2)	0.0026 (5)	0.2505 (3)	0.2530 (6)	1.30 (13)
S(3)	0.2446 (5)	0.1251 (2)	0.2574 (5)	0.90 (12)
S(4)	0.2518 (5)	0.0015 (3)	0.5073 (5)	0.81 (12)
S(5)	0.0016 (5)	0.1271 (3)	0.4963 (6)	1.08 (13)
S(6)	-0.0066 (5)	0.1229 (3)	-0.0077 (5)	0.88 (12)
S(7)	0.2545 (5)	0.1217 (2)	0.7475 (5)	0.94 (12)
S(8)	0.2452 (5)	0.2476 (3)	0.4963 (5)	0.98 (12)
M(1)	0.1331 (4)	0.0573 (2)	0.3688 (3)	2.41 (9)
M(2)	0.1053 (4)	0.0619 (2)	0.6223 (4)	3.17 (11)
M(3)	0.3912 (4)	0.0593 (2)	0.3708 (4)	2.74 (10)
M(4)	0.3766 (3)	0.0598 (2)	0.6318 (3)	1.79 (8)
M(5)	0.1192 (3)	0.1901 (2)	0.3727 (3)	1.84 (8)
M(6)	0.1248 (4)	0.1871 (2)	0.6440 (4)	2.77 (10)
M(7)	0.3777 (4)	0.1906 (2)	0.3588 (4)	2.86 (10)
M(8)	0.3804 (4)	0.1934 (2)	0.6170 (4)	2.38 (9)
M(9)	0.1442 (4)	0.0698 (2)	0.8917 (4)	3.25 (11)
M(10)	0.3424 (5)	0.0790 (2)	0.0963 (5)	3.99 (13)
M(11)	0.1409 (4)	0.1761 (2)	0.1014 (4)	3.48 (11)
M(12)	0.3495 (5)	0.1771 (2)	0.8990 (5)	3.79 (12)

All computations in the present investigation were carried out at the Computing Centre of Osaka University with the UNICS system (Sakurai, 1967).

Description

A part of the structure is shown in Fig. 7. Sulphur atoms occupy approximately the nodes of a cubic

* A list of observed and calculated structure factors for superstructure reflexions has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31018 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

face-centred lattice and metal atoms occupy in an ordered way the interstices between the sulphur atoms. The characteristic feature of the structure of bornite is the arrangement of metal atoms. The supercell of bornite consists of $2 \times 4 \times 2$ cubes of face-centred cell of $a' \sim 5.5$ Å, each of which corresponds to the cell of high bornite. Ordered arrangements of metal atoms

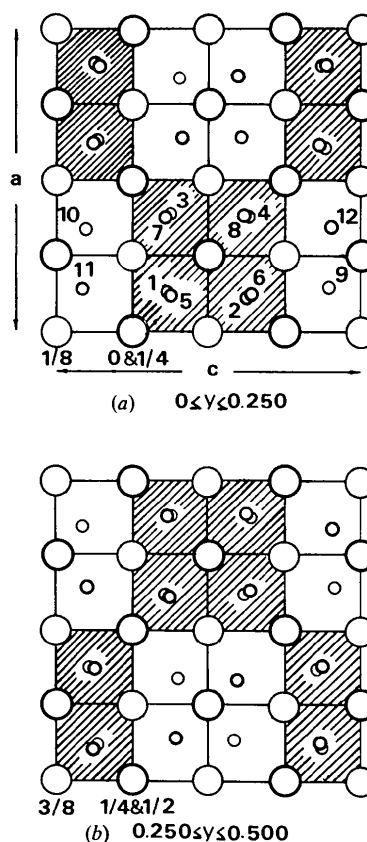


Fig. 7. The structure from $y=0$ to 0.5 of the unit cell of bornite. Sulphur atoms are represented by large circles and metal atoms by small circles, respectively. The approximate y parameters are given for the sulphur atoms. The numbering of the metal atoms corresponds to that in Table 1. The hatched part is the antifluorite-type cube and the other, the sphalerite-type cube.

Table 2. Metal(M)-sulphur(S) distances (Å) in the sulphur tetrahedron in bornite

	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	S(7)	S(8)	Mean
M(1)	2.271		2.275	2.341	2.520				2.352
M(2)	2.253			2.430	2.286				2.368
M(3)	2.265		2.487	2.482		2.331	2.502		2.391
M(4)	2.271			2.313		2.322	2.286		2.298
M(5)		2.256	2.344		2.321			2.306	2.307
M(6)		2.253			2.481		2.312	2.472	2.380
M(7)		2.255	2.325			2.541		2.434	2.389
M(8)		2.307				2.310	2.530	2.313	2.365
M(9)	2.737			2.309		2.300	2.288		2.409 (2.297)
M(10)	2.979		2.296	2.261	2.274				2.453 (2.277)
M(11)		2.774	2.335			2.321		2.325	2.439 (2.327)
M(12)		2.843			2.299		2.302	2.269	2.428 (2.290)

* Calculated errors are 0.007 Å for all M-S distances. The mean values of three shortest distances are in parentheses.

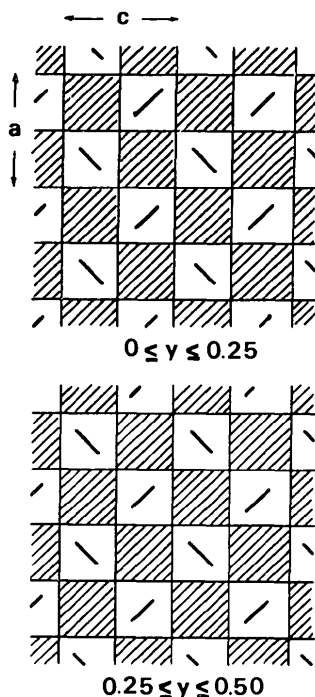


Fig. 8. A mosaic pattern structure of the antiferite-type cubes (the hatched part) and the sphalerite-type cubes of bornite. Two different orientations of the sphalerite-type cubes are shown based on the orientation of the arrangement of vacant tetrahedra of sulphur atoms.

result in the two different types of cubes. One is the antiferite type with eight metal atoms at the tetrahedral sites and the other is the sphalerite-type cube in which only four metal atoms are present as in the sphalerite structure (Fig. 7). The vacant sulphur tetrahedra for metal atoms concentrate in the sphalerite-type cube and result in a unique clustering of vacancies for metal atoms in bornite. The two types of cubes alternate along the *a*, *b* and *c* directions, forming a characteristic three-dimensional mosaic pattern (Fig. 8).

The metal atoms have essentially two different coordinations of sulphur atoms: tetrahedral and trigonal. In the antiferite-type cube, the metal atoms have tetrahedral coordination. However, they are slightly displaced from the centres towards one of the triangles or one of the edges of the tetrahedra, giving three short and one slightly long, or two short and two slightly long M–S distances, respectively (Table 2). The shortest M–M distance in the antiferite-type cube is 2.755 Å between M(2) and M(6).

On the other hand, four metal atoms in the sphalerite-type cube are markedly displaced from the

centres of the tetrahedra to the triangles. Actually M(10) has a trigonal coordination, *i.e.*, the sum of the angles around M(10) is close to 360°. These displacements make one of the M–S distances in the sulphur tetrahedra more than 2.737 Å (Table 2). The shortest M–M distance in the sphalerite-type cube is 3.045 Å between M(10) and M(12).

There are two sites for the Fe atom in the asymmetric unit if Cu and Fe are completely ordered. Tetrahedral coordination around Fe is generally regular in sulphide minerals (Hall & Stewart, 1973). On the other hand, coordination around Cu is often distorted (Koto & Morimoto, 1970). The Cu–S bond distance is longer than that of the Fe–S distance. Therefore the most probable sites for the iron atoms are M(4) and M(5) whose average M–S distances (2.298 and 2.307 Å, respectively) are the shortest and whose tetrahedral coordinations are the most regular.

In the structure of the high form of bornite, metal atoms are statistically distributed in the interstices between sulphur atoms of the antiferite structure (Morimoto, 1964). Through the transition to the low form of bornite, however, a characteristic ordered arrangement of metal atoms appears with some displacements of the metal and sulphur atoms from ideal tetrahedral sites and nodes of face-centred lattice, respectively.

References

- ALLAIS, G. (1968). *Bull. Soc. Fr. Minér. Crist.* **91**, 600–620.
 BUERGER, M. J. (1956). *Proc. Natl. Acad. Sci. U.S.A.* **42**, 776–781.
 FRUEH, A. J. JR (1950). *Amer. Min.* **35**, 185–192.
 FRUEH, A. J. JR (1953). *Acta Cryst.* **6**, 454–456.
 HALL, S. R. & STEWART, J. M. (1973). *Acta Cryst.* **B29**, 579–585.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KOTO, K. & MORIMOTO, N. (1970). *Acta Cryst.* **B26**, 915–924.
 KOTO, K. & MORIMOTO, N. (1972). *Acta Cryst.* **A28**, S70.
 LUNDQVIST, D. & WESTGREN, A. (1936). *Ark. Kem.* **12 B**, 1–6.
 MARUMO, F. (1967). *Z. Kristallogr.* **124**, 352–368.
 MORIMOTO, N. (1964). *Acta Cryst.* **17**, 351–360.
 MORIMOTO, N. & KULLERUD, G. (1961). *Amer. Min.* **46**, 1270–1282.
 SAKURAI, K. (1958). *Acta Cryst.* **11**, 840–842.
 SAKURAI, T. (1967). UNICS System. Cryst. Soc. Japan.
 TAKÉUCHI, Y. (1972). *Z. Kristallogr.* **135**, 120–136.
 TAKÉUCHI, Y. & HORIUCHI, H. (1972). *Z. Kristallogr.* **135**, 93–119.
 TUNELL, G. & ADAMS, C. E. (1949). *Amer. Min.* **34**, 824–829.