

Structures of Two Polymorphic Forms of  $\text{Cu}_5\text{FeS}_4$ 

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There exist three polymorphic forms of  $\text{Cu}_5\text{FeS}_4$ . All three can be obtained by starting with natural or synthetic material. A high-temperature form, stable above  $228 \pm 5$  °C, changes to a transitional metastable form on cooling below  $228 \pm 5$  °C; it then gradually changes to the low-temperature form. Only the latter occurs in nature, as bornite.

The crystal structure of the high-temperature form was determined from single-crystal data. The cubic cell with  $a = 5.50$  Å contains  $\text{Cu}_5\text{FeS}_4$ . The space group is  $Fm\bar{3}m$ . The S atoms occupy the nodes of the face-centered cubic lattice. In each tetrahedron of S atoms, the metal atom is statistically distributed among 24 equivalent sites with coordinates  $x = 0.310$ ,  $y = 0.290$ , and  $z = 0.270$ , the total metal atom in the tetrahedron being  $\frac{2}{3}$  (Cu, Fe).

The crystal structure of the metastable form of synthetic bornite was also determined from single-crystal data. The space group is  $Fd\bar{3}m$ , with  $a = 10.94$  Å, but the cubic symmetry results from the twinning of small domains with rhombohedral symmetry in eight different orientations. Each individual in this twin has space group  $R\bar{3}m$ , with  $a_{rh} = 6.70$  Å and  $\alpha = 33^\circ 32'$ . In this rhombohedral structure all the sulfur atoms remain in cubic close-packing. The metal atoms are situated in three out of every four tetrahedra; they are statistically distributed among four equivalent sites inside each occupied tetrahedron. No distinction was made between Cu and Fe atoms, either in the metastable structure or in the high-temperature structure.

The low-temperature form shows space group  $P\bar{4}_2c$  with  $a = 10.94$  and  $c = 21.88$  Å.

A structural mechanism is proposed for the polymorphic transition between the high-temperature and the metastable forms.

## Introduction

The chemical composition of natural bornite was first established by Harrington (1903) as  $\text{Cu}_5\text{FeS}_4$ ; it was confirmed by Allen (1916), and Zies & Merwin (1955).

The first attempt to determine the crystal structure of bornite by X-ray methods was made by de Jong (1928), who used natural bornite. He proposed a structure based on a cubic cell with  $a = 10.910 \pm 0.005$  kX. The structure was, however, in marked discord with the observed intensities. Lundqvist & Westgren (1936) studied the structure of synthetic material by means of powder photographs. They gave a cubic cell with  $a = 10.94$  kX and space group  $Fd\bar{3}m (O_h^h)$ . Their structure was based on cubic close-packing of sulfur atoms, with metal atoms in the interstices. Several distributions of metal atoms were suggested, but none of them could be confirmed by X-ray intensity data. Tunell & Adams (1949) examined crystals of 'bornite' from the Carn Brea Mine, Illogan, Cornwall, and reported a cubic cell with  $a = 32.8$  Å. They proposed a structure that gave reasonable agreement for all the reflections of strong and medium intensities. A considerable number of weak reflections, on the other hand, remained unaccounted for.†

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† The crystals studied by Tunell and Adams were recently re-examined in detail. They consist of at least two phases: the low-temperature bornite and a new phase with tetragonal symmetry (Morimoto, Greig & Tunell, 1960).

Before determining the crystal structure of bornite, it is necessary to elucidate its polymorphic relationships and to explain the conflicting literature data on synthetic and natural bornites.

Polymorphic relations of  $\text{Cu}_5\text{FeS}_4$ 

Morimoto & Kullerud (1961) used the high-temperature single-crystal X-ray method to study synthetic bornites cooled from various temperatures and natural bornites from different localities. They found two stable forms and one transitional metastable form. The high-temperature form is cubic with  $a = 5.50 \pm 0.01$  Å,  $Z = 1$ , diffraction aspect  $F^{***}$ ; the transitional metastable form is also cubic with  $a = 10.94$  Å,  $Z = 8$ , diffraction aspect  $Fd^{**}$ ; and the low-temperature form is tetragonal with  $a = 10.94$ ,  $c = 21.88$  Å, space group  $P\bar{4}_2c$ .

Various cell dimensions and symmetries found on specimens of natural bornite, such as those of Frueh (1950) and Kullerud, Donnay & Donnay (1960), were explained by twinning of the low-temperature form, the twin operation being a  $120^\circ$  rotation about the row  $[221]$  of the tetragonal lattice, that is the body diagonal of the cubic cell (Morimoto & Kullerud, 1961).

The high-temperature form is unquenchable. When it is cooled to below  $228 \pm 5$  °C it instantly changes to the metastable form. The latter gradually transforms to the low-temperature form in about a week at room temperature. The easy transitions among the

polymorphic forms and the simple relations between their cells suggest that their structures should be closely related to one another.

### Crystal structure of the high-temperature form

Because the high-temperature form is unquenchable, X-ray intensity data were obtained on the Buerger precession camera, modified for high-temperature use (Morimoto & Kullerud, 1961).

Crystals  $0.05 \times 0.05 \times 0.05$  mm<sup>3</sup> in size, synthesized at 900 °C by Kullerud, were used for the structure determination. The photographs of  $(1\bar{1}0)_0^*$  (the zero layer perpendicular to  $[1\bar{1}0]$ ) were taken at  $240 \pm 5$  °C with various exposure times and Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å). The relative intensities of the reflections  $hhl$  were obtained photometrically. They were converted to an absolute scale in the course of the structure analysis, in order to make  $\Sigma|F_o| = \Sigma|F_c|$ . No correction was made for absorption or extinction.

The cell of the high-temperature form contains one formula unit of  $\text{Cu}_5\text{FeS}_4$ . Cu and Fe atoms are dealt with as metal atoms, without distinction, in this structure determination because of the small difference between their scattering factors. The sulfur atoms were assumed to occupy the nodes of the cubic face-centered lattice with  $a = 5.50$  Å. An anti-fluorite structure, in which the six metal atoms statistically occupy the centers of the eight tetrahedra of sulfur atoms, was first examined. The calculated  $F$  values are too large for the reflections with all indices even, and too small for those with all indices odd (Table 1, column 1).

Table 1. Comparison of observed and calculated  $F$  values for the high-temperature form

$hkl$	$F_o$	(1)	(2)
		Anti-fluorite structure (statistical distribution)	Final structure
0 0 2	54	60.5	-54.7
4	50	63.5	52.0
6	—	18.0	7.4
1 1 1	42	30.0	44.0
3	34	19.7	32.3
5	21	11.6	15.1
2 2 0	92	87.5	98.2
2	24	35.4	-14.9
4	37	49.8	32.7
3 3 1	18	14.2	19.7
3	27	18.6	30.4
5	—	7.9	6.0
4 4 0	22	39.4	21.0
2	—	15.4	9.7
4	—	25.5	10.5

On the basis of the cubic close-packing of the sulfur atoms, two models are possible. In one of them the metal atoms are confined inside the tetrahedra of the sulfur atoms and they can be distributed not

only at the centers of, but also over several equivalent sites in, the sulfur tetrahedra. The other model is a so-called 'average structure', like that of  $\alpha\text{-AgI}$  (Strock, 1934, 1935). The metal atoms are distributed not only inside, but also outside, the tetrahedra, at the centers of triangles or octahedra of sulfur atoms.

In the first model the metal atoms were statistically distributed among various sites symmetrically arranged about the centers of the sulfur tetrahedra. The number of metal atoms in each sulfur tetrahedron was made to vary from one to one-half, keeping the cubic symmetry. Good agreement between observed and calculated  $F$  values has been obtained when three-fourths of a metal atom is statistically distributed over 24 equivalent sites in each sulfur tetrahedron (Table 1, column 2). The coordinates of the metal atoms in general position are  $x = 0.310$ ,  $y = 0.290$ , and  $z = 0.270$ . The scattering factors of the metal atoms were calculated from those of Cu and Fe atoms given by Hartree. The temperature factors used for calculation are  $B = 4.5$  for the metal atoms and  $B = 2.0$  for the sulfur atoms. The  $R$  index for eleven observed reflections is 0.09 (excluding non-observed reflections). In the structure obtained (Fig. 1) the distances from one of the metal sites to the sulfur atoms are 2.92, 2.42, 2.29, and 2.15 Å.

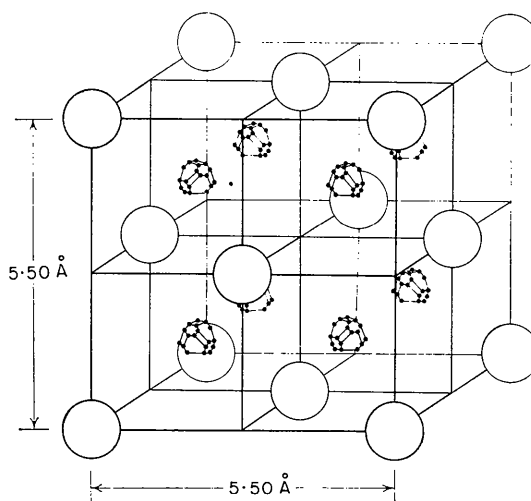


Fig. 1. Structure of the high-temperature form: sulfur atoms (white circles) and metal atoms (black dots).

Attempts to move some metal atoms outside the sulfur tetrahedra (second model) did increase discrepancies between the observed and calculated  $F$  values.

The structure of the high-temperature form is thus essentially the anti-fluorite structure, only slightly more complicated. The sulfur atoms occupy the nodes of the cubic face-centered lattice. Each tetrahedron of sulfur atoms, on the average, contains  $\frac{3}{4}$  of a metal atom. This fractional atom is itself statistically distributed over 24 equivalent sites inside the sulfur tetrahedron. In the whole 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. 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 dynamical state of the metal atoms.

### Crystal structure of the metastable form

Synthetic specimens quenched in water from 900 °C were used to collect intensity data. Crystals were approximately  $0.05 \times 0.05 \times 0.1$  mm<sup>3</sup> in size. Weissenberg photographs were taken with Mo  $K\alpha$  radiation around the rows [100] and [110], up to the 4th-layers, with multiple-film technique. Relative intensities were estimated visually, and the Lorentz and polarization corrections were applied. Neither extinction nor absorption correction was made. The relative values of structure factors were put on the absolute scale at a later stage of the analysis.

Any structure proposed for the metastable form should explain two characteristics of the intensity distribution. One is the existence of a cubic sub-cell with  $a' = a/2 = 5.47$  Å, which gives much stronger intensities to the reflections with  $h, k,$  and  $l$  all even than to those with  $h, k,$  and  $l$  all odd. The other is a special extinction rule: the absence of reflections other than those for which  $h, k,$  and  $l$  are all odd, all 2 mod. 4, or all 0 mod. 4.

Two different approaches to the structure analysis are possible. One is to find the positions of 40Cu, 8Fe, and 32S atoms in the cell of  $a = 10.94$  Å with space group  $Fd\bar{3}m$ . The most reasonable method to do this is to find the distribution of the metal atoms, keeping the sulfur atoms at the origin and at the face centers of the sub-cell (positions 16:c and 16:d). This was the procedure followed by Lundqvist & Westgren (1936) and by Tunell & Adams (1949). Following the method developed by Morimoto, Marumo & Sadanaga (1962), various structure models with cubic symmetry, which could explain the special extinction rule, were examined on the assumption that all metal atoms are statistically distributed in the interstices of the cubic close-packing of the sulfur atoms. The calculated  $F$  values for the reflections with  $h, k,$  and  $l$  odd, in these models, are equal to about one-half of the observed values, as long as the number of metal atoms enclosed in a sulfur tetrahedron does not exceed one. Thus all attempts along this line failed to give a reasonable structure, suggesting that the true symmetry is lower than cubic.

The other way to start the analysis is to use a twin hypothesis, assuming a lower symmetry for the true cell of the metastable form. Such a twin hypothesis was proposed for digenite by Donnay, Donnay & Kullerud (1958), to explain special extinction rules.

#### *Twinning and true cell*

The procedures of Donnay, Donnay & Kullerud (1958) on digenite have been followed in order to find

the true cell of the metastable form on the basis of the twin hypothesis.

The observed point group  $m\bar{3}m$  is considered to be generated by the combination of the twin operations with the symmetry operations of the individual crystals. If the individual crystals are assumed to be rhombohedral in order to explain the observed special extinction rule, the twin relations (Table 2) differ according to the point group of the individual crystals.

Table 2. Possible twin relations in the metastable form

Symmetry of individual crystals	Twin elements	Number of individual crystals	Symmetry of complete twin
$\bar{3}m$	4	4	$m\bar{3}m$
$3m$	$4/m$	8	$m\bar{3}m$
	4	4	$4\bar{3}m$
32	$4/m$	8	$m\bar{3}m$
	4	4	432
$\bar{3}$	$41m$	8	$m\bar{3}m$
3	$4/m1m$	16	$m\bar{3}m$
	$41m$	8	$4\bar{3}m$
	412	8	432

As described later, the individual crystals must have point group  $3m$  on the basis of the structure analysis. Thus, if the point group of the twin is truly  $m\bar{3}m$ , the twin operations are the seven operations other than identity in any of the three  $4/m$  symmetry subgroups of the twin. The twin relations obtained are shown (Fig. 2) in stereographic projection.

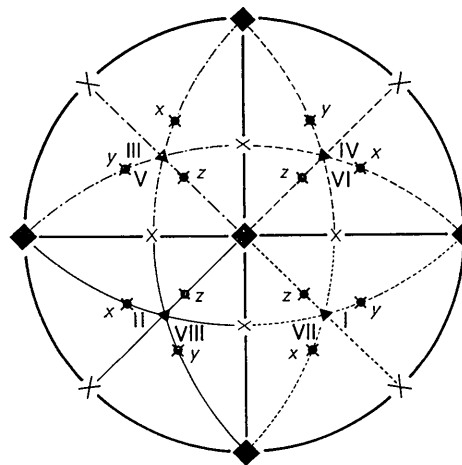


Fig. 2. Stereographic projection on  $(001)_c$  of the twin in the metastable form.

Because the twin lattice extends without deviation throughout the twin edifice, the twin obliquity (*International Tables for X-ray Crystallography*, 1959, vol. II, p. 104) is zero. The twin axis is  $[\bar{1}\bar{1}\bar{3}]$ , referred to the rhombohedral axes of the crystal. The twin index is 2. This twin arrangement gives the  $s$  matrices (*International Tables for X-ray crystallography*, 1952,

Table 3. Transformations of indices

Crystal I			Crystal II			Crystal III			Crystal IV		
Matrices <i>s</i> : rhombohedral ( <i>pqr</i> ) from cubic ( <i>hkl</i> )*											
·50	·25	·25	·25	· $\bar{5}0$	·25	· $\bar{5}0$	· $\bar{2}5$	·25	· $\bar{2}5$	·50	·25
·25	·50	·25	·50	· $\bar{2}5$	·25	· $\bar{2}5$	·50	·25	· $\bar{5}0$	·25	·25
·25	·25	·50	·25	· $\bar{2}5$	·50	· $\bar{2}5$	· $\bar{2}5$	·50	· $\bar{2}5$	·25	·50
Matrices <i>t</i> : cubic ( <i>hkl</i> ) from rhombohedral ( <i>pqr</i> )*											
$\bar{3}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{3}$	$\bar{1}$
$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{1}$
$\bar{1}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{1}$	$\bar{3}$	$\bar{1}$	$\bar{1}$	$\bar{3}$

\* To obtain the matrices for crystals V–VIII, change the signs of numbers in the matrices for crystals I–IV respectively.

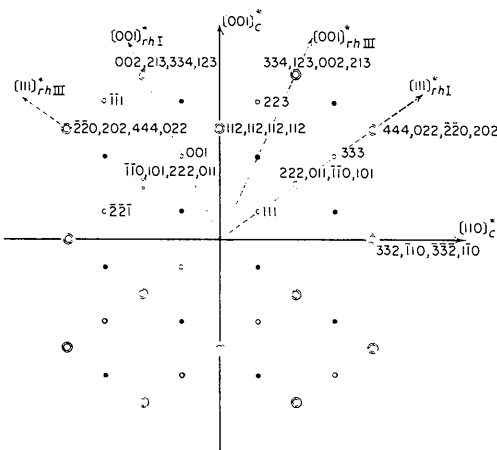


Fig. 3. Precession pattern  $(1\bar{1}0)_c^*$ , indexed with reference to the rhombohedral axes of the eight individuals of the twin. Empty circles are reflections of crystals I and V; black circles, of crystals III and VII. Double circles are reflections that belong to all eight crystals; they are indexed in crystals I to IV in sequence, the indices for crystals V to VIII being omitted for simplicity.

*hkl*, one matrix for each of the eight individual crystals I to VIII. The inverse *t* matrices, also given in Table 3, permit us to obtain *hkl* from *pqr*. Fig. 3 is the precession pattern indexed with reference to the rhombohedral axes of the individual crystals in the twin. For simplicity the reflections from only four individuals are given. Other reflections with indices of opposite signs are omitted.

Thus the true cell of the metastable form is rhombohedral. The diffraction aspect is  $R^{**}$ . The cell dimensions, referred to hexagonal axes are:  $a_{\text{hex}} = a_c/2/4 = 3.87 \text{ \AA}$ ,  $c_{\text{hex}} = a_c/3 = 18.95 \text{ \AA}$ ,  $(c/a)_{\text{hex}} = 4.90$ ,  $V_{\text{hex}} = 3a_c^3/16 \text{ \AA}^3$ . Since the large cubic cell contains  $8\text{Cu}_5\text{FeS}_4$ , the hexagonal cell contains  $\frac{3}{2}\text{Cu}_5\text{FeS}_4$ . The rhombohedral cell has dimensions

$$a_{\text{rh}} = \left(\frac{1}{3}\right)^{1/2}(c_{\text{hex}}^2 + 3a_{\text{hex}}^2) = 6.70 \text{ \AA}, \quad \alpha = 33^\circ 32'.$$

Fig. 4 shows the relationship between the cubic cell and the rhombohedral cell. The rhombohedral cell has only 1/16 of the volume of the cubic cell, and contains  $(\text{Cu,Fe})_3\text{S}_2$ , where the atomic ratio Cu:Fe is equal to 5:1. Because of the small difference between the atomic scattering factors of Cu and Fe, we did not attempt to locate Fe and Cu atoms separately.

#### Determination of the atomic coordinates

According to the translation group *R* of the crystal derived from the study of twinning, the possible space groups are  $R\bar{3}m$ ,  $R3m$ ,  $R32$ ,  $R\bar{3}$ , and  $R3$ . Because of the steepness of the rhombohedral cell, all the atoms should be placed in special positions  $(x, x, x)$  on the threefold axis or should be statistically distributed on sites close to the threefold axis.

The  $(c/a)_{\text{hex}}$  ratio stays exactly equal to  $\sqrt{24}$ ; not the slightest deviation from this value was observed even in the powder patterns, so that cubic symmetry must be assigned to the metastable form. This suggests that the sulfur atoms throughout the structure remain at the nodes of the face-centered lattice with  $a = 5.47 \text{ \AA}$ , as in the high-temperature form. The analysis was, therefore, started on the assumption that all the sulfur atoms occupy exactly the same sites as in the high-temperature form. In the rhombohedral cell they lie at  $0, 0, 0$  and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ .

Let  $s = p + q + r$ . The contributions of the two sulfur

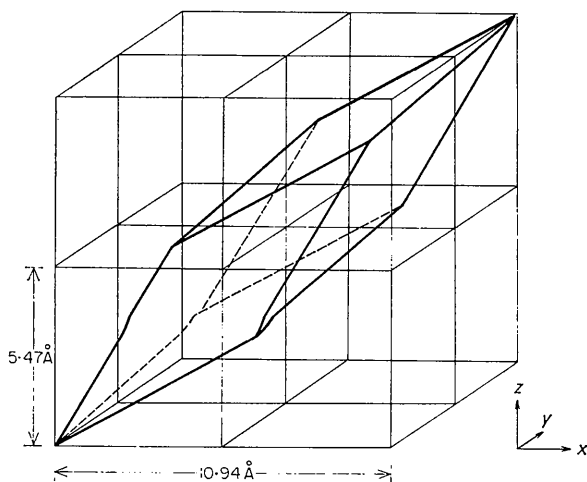


Fig. 4. Relationship between the cubic cell and the rhombohedral cell.

vol. I, p. 15), listed in Table 3, that must be used to obtain rhombohedral indices *pqr* from cubic ones

Table 4. Observed  $U_s = F_s/f_M$  when  $s = p + q + r$  is odd

s:	1	3	5	7	9	11	13	15	17	19	21
	$\begin{matrix} U \\ pqr \\ 001 \end{matrix}$	$\begin{matrix} U \\ pqr \\ (111) \end{matrix}$	$\begin{matrix} U \\ pqr \\ 22\bar{1} \end{matrix}$	$\begin{matrix} U \\ pqr \\ 223 \end{matrix}$	$\begin{matrix} U \\ pqr \\ 333 \end{matrix}$	$\begin{matrix} U \\ pqr \\ 443 \end{matrix}$	$\begin{matrix} U \\ pqr \\ 445 \end{matrix}$	$\begin{matrix} U \\ pqr \\ 555 \end{matrix}$	$\begin{matrix} U \\ pqr \\ 665 \end{matrix}$	$\begin{matrix} U \\ pqr \\ 667 \end{matrix}$	$\begin{matrix} U \\ pqr \\ 777 \end{matrix}$
	1.24	(0.15)*	1.39	0.29	1.80	0.54	1.58	1.54	1.89	0	1.54
	1.11	0.95	1.98	0	1.60	0	0.85	0.72	1.89	0	1.54
	1.80	0.03	1.45	0	1.66	0	0.85	0.72	1.89	0	1.54
	1.49	0.19	1.57	0	1.66	0	0.85	0.72	1.89	0	1.54
	1.11	0.93	1.79	0	1.37	0	1.32	0.72	1.39	0	1.54
	1.36	1.04	1.43	0.07	1.66	0.18	1.25	0.88	1.73	0	1.54
No. of reflections	5	4	5	4	5	3	3	2	3	1	1

\* The observed value of (111) is presumed to be incorrect because of extinction, and has been omitted from the calculation of the mean value.

atoms to the reflections with  $s$  odd, therefore, cancel each other. If we put  $U_s = F_s/f_M$  for any reflection with  $s$  odd ( $f_M$  represents the scattering factor of the metal atom), the values of  $U_s$  should be constant for any given value of  $s$  in any possible space group, provided the metal atoms occupy special positions  $(x, x, x)$ . In the  $U_s$  values (Table 4) the temperature factor  $B=1.0$  was applied to obtain  $f_M$ . Although  $U_s$  values stay fairly constant for constant  $s$ , their fluctuations are large enough to show a statistical distribution of metal atoms over the sites of a general position  $(x, y, z)$ .

At the earlier stage of the structure analysis, however, the three metal atoms are assumed to lie on the threefold axis. The special position  $(x, x, x)$  is of multiplicity two in space groups  $R\bar{3}m$ ,  $R\bar{3}$ , and  $R32$  and is of multiplicity one in space groups  $R3m$  and  $R3$ . Permitting a partial distribution of metal atoms in the former space groups, it is only necessary to consider two space groups  $R\bar{3}m$  and  $R3m$  as representatives of two groups with different multiplicities. Then the reflections with  $s$  even are superpositions of four or eight reflections with the same or with different indices, diffracted from different individuals of the twin. For the convenience of comparison, hypothetical calculated and observed structure factors were adopted for each reflection with  $s$  even as follows:

$$F_{hkl}(\text{calc.}) = \sqrt{\sum_{i=1}^4 F_{piqiri}^2}$$

$$F_{hkl}(\text{obs.}) = K\sqrt{(I_{hkl}\text{Obs.})}$$

where  $piqiri$  refers to the reflection  $pqr$  of the  $i$ th crystal of the twin and  $p, q$ , and  $r$  are related to  $h, k$ , and  $l$  by the matrices of Table 3.\*

For an edifice constructed on the basis of crystal symmetry  $R\bar{3}m$ , the calculated  $F$  values are larger than the observed ones for  $s=4n$ , and smaller for

Table 5. Atomic coordinates in metastable form

Atom*	No. of equivalent sites	Fraction of atom	$x$	$y$	$z$
S <sub>I</sub>	1	1	0	0	0
S <sub>II</sub>	1	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
M <sub>I</sub> (a)	1	$\frac{1}{4}$	0.155	0.155	0.155
M <sub>I</sub> (b)	3	$\frac{3}{4}$	0.115	0.115	0.195
M <sub>II</sub> (a)	1	$\frac{1}{4}$	0.365	0.365	0.365
M <sub>II</sub> (b)	3	$\frac{3}{4}$	0.405	0.405	0.325
M <sub>III</sub> (a)	1	$\frac{1}{4}$	0.635	0.635	0.635
M <sub>III</sub> (b)	3	$\frac{3}{4}$	0.595	0.595	0.675

\* M<sub>I</sub>(a) and (b), M<sub>II</sub>(a) and (b), and M<sub>III</sub>(a) and (b) make tetrahedral arrangements, the centers of which are respectively: (0.145, 0.145, 0.145), (0.375, 0.375, 0.375), and (0.625, 0.625, 0.625).

\* When the twin comprises eight individuals, the following relation exists:

$$F_{piqiri}^2 = F_{pi+4qi+4ri+4}^2$$

Thus the formulae mentioned above are used regardless of twin types.

Table 6. Comparison of observed and calculated  $F$  values for the metastable form

Cubic h k l	Rhombohedral				$F_o/2$	$F_c/2$
	$F_1^*F_1^*$ &	$F_2^*F_2^*$ &	$F_3^*F_3^*$ &	$F_4^*F_4^*$ &		
	$F_5^*F_5^*$	$F_6^*F_6^*$	$F_7^*F_7^*$	$F_8^*F_8^*$		
(a) Reflections produced by all eight crystals in the twin						
0 0 4	1 1 2	1 1 2	1 1 2	1 1 2	81	87.2
8	2 2 4	2 2 4	2 2 4	2 2 4	90	93.6
12	3 3 6	3 3 6	3 3 6	3 3 6	11	15.4
2 2 2	2 2 2	0 1 1	$\bar{1} \bar{1} 0$	1 0 1	68	65.4
6	3 3 4	1 2 3	0 0 2	2 1 3	45	46.6
10	4 4 6	2 3 5	1 1 4	3 2 5	22	27.5
14	5 5 8	3 4 7	2 2 6	4 3 7	18	17.6
4 4 0	3 3 2	$\bar{1} 1 0$	$\bar{2} \bar{2} \bar{2}$	1 $\bar{1} 0$	126	139.0
4	4 4 4	0 2 2	$\bar{2} \bar{2} 0$	2 0 2	54	56.4
8	5 5 6	1 3 4	$\bar{1} \bar{1} 2$	3 1 4	73	75.2
12	6 6 8	2 4 6	0 0 4	4 2 6	-	11.6
6 6 2	5 5 4	$\bar{1} 2 1$	$\bar{4} \bar{4} \bar{2}$	2 $\bar{1} 1$	24	33.3
6	6 6 6	0 3 3	$\bar{4} \bar{4} 0$	3 0 3	40	40.0
10	7 7 8	1 4 5	$\bar{2} \bar{2} 2$	4 1 5	13	13.7
8 8 0	6 6 4	$\bar{2} 2 0$	$\bar{6} \bar{6} \bar{4}$	2 $\bar{2} 0$	54	61.0
4	7 7 6	$\bar{1} 3 2$	$\bar{5} \bar{5} \bar{2}$	3 $\bar{1} 2$	14	16.9
8	8 8 8	0 4 4	$\bar{4} \bar{4} 0$	4 0 4	34	33.6
0 4 8	3 4 5	0 1 3	1 0 3	4 3 5	28	35.6
12	4 5 7	1 2 5	2 1 5	5 4 7	38	44.0
2.6.10	5 6 7	0 2 4	0 $\bar{1} 3$	5 3 6	29	27.0
(b) Reflections produced by two crystals in the twin						
1 1 1	1 1 1				4	14.9
3			0 0 1		30	26.6
5	2 2 3				6	3.6
7			1 1 3		33	24.2
9	3 3 5				-	8.0
11			2 2 5		17	15.3
3 3 1			$\bar{2} \bar{2} \bar{1}$		31	32.8
3	3 3 3				37	38.8
5			$\bar{1} \bar{1} 1$		20	18.6
7	4 4 5				23	29.0
9			0 0 3		13	6.1
11	5 5 7				18	17.1
5 5 1	4 4 3		$\bar{3} \bar{3} \bar{1}$		9	13.5
3					-	1.8
5	5 5 5		$\bar{2} \bar{2} 1$		17	14.9
7					14	6.3
9	6 6 7		$\bar{1} \bar{1} 3$		-	11.7
11					9	6.5
7 7 1			$\bar{5} \bar{5} \bar{3}$		10	21.6
3	6 6 5				21	22.0
5			$\bar{4} \bar{4} \bar{1}$		14	15.7
7	7 7 7		$\bar{3} \bar{3} 1$		15	16.7
9					6	8.1
1 3 1		$\bar{1} 0 0$			30	26.6
3				2 1 2	31	32.8
5		0 1 2			18	11.3
7		1 2 4		3 2 4	25	27.5
9					-	1.6
11		2 3 6		4 3 6	13	16.7
13					-	4.3
1 5 1	2 3 2		$\bar{1} \bar{2} 0$		6	3.6
3					18	11.3
5	3 4 4		0 $\bar{1} 2$		9	13.5
7					25	13.5
9	4 5 6		1 0 4		6	11.5
11					14	10.4
13	5 6 8				-	7.8
1 7 1		$\bar{3} \bar{1} \bar{1}$			33	24.2
3				4 2 3	25	27.5
5		$\bar{2} 0 1$			25	13.5
7				5 3 5	10	21.6
9		$\bar{1} 1 3$			9	4.7
11				6 4 7	11	13.1
3 5 1		$\bar{1} 1 1$		2 0 1	18	11.3
3					20	18.6
5		0 2 3		3 0 3	-	1.8
7					19	17.8
9		1 3 5		4 2 5	-	7.6
11					16	12.7

$s=4n+2$ . To bring the calculated  $F$  values to agree with the observed ones for both kinds of reflections, we have to choose space group  $R3m$ . The calculated  $F$  values for the reflections with  $s$  odd also support the choice of  $R3m$ .

As long as the metal atoms are kept on the threefold axis,  $F_{662}(\text{calc.})$  is always larger than  $F_{666}(\text{calc.})$  contrary to observation. To avoid this discrepancy and to explain the fluctuations of the  $U_s$  values with constant  $s$ , the metal atoms are statistically distributed around the positions which were determined on the assumption that all metal atoms remain on the threefold axis. The best agreements were obtained when each metal atom was distributed tetrahedrally. In  $R3m$  this can be done by placing  $\frac{1}{4}$  atom in position  $1a$  and  $\frac{3}{4}$  atom in position  $3b$ .

Attempts to obtain a structure on the basis of space group  $R3$  with more complicated twin relations did not lead to any improvement.

The atomic coordinates of the final structure are given in Table 5. The calculated  $F$  values are compared with the observed ones in Table 6. The atomic scattering factors for the metal atoms are calculated for the atomic ratio Cu:Fe=5:1 using the values of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for Cu and those of Freeman & Wood (1959) for Fe. The scattering factors for sulfur atoms are taken from Viervoll & Øgrim (1949). The temperature factor  $B=1.0$  is applied both to metal and to sulfur. The  $R$  index, excluding non-observed reflections, is 0.09 for the reflections with  $s$  even, 0.25 for those with  $s$  odd, and 0.15 considering all observed reflections.

Attempts to refine the atomic coordinates obtained above by the usual trial and error method are hampered because of the superposition by twinning of reflections with  $s$  even. No estimation of the accuracy of atomic coordinates was made.

#### Discussion of the structure

The structure of the (rhombohedral) metastable form (Fig. 5(b)) can be derived from that of the (cubic) high-temperature form (Fig. 5(a)). All the sulfur atoms stay in place, retaining cubic close-packing. Of the four partial metal atoms in sulfur tetrahedra in the high-temperature form, two remain in their tetrahedra. One tetrahedron becomes vacant, and the metal  $\frac{3}{4}$  atom which occupied it in the high-temperature form is redistributed among the other three sulfur tetrahedra, which now contain one full metal atom apiece. To compensate for the vacant tetrahedron, the last metal  $M_I$  moves slightly inside its tetrahedron. The statistical distribution of three-fourths of a metal among 24 sites inside each sulfur tetrahedron changes to the statistical distribution of one metal atom among four sites.

The rhombohedral structure of the metastable form, drawn by means of a hexagonal cell (Fig. 6(b)), is compared with the rhombohedral cell (Fig. 6(a)) to

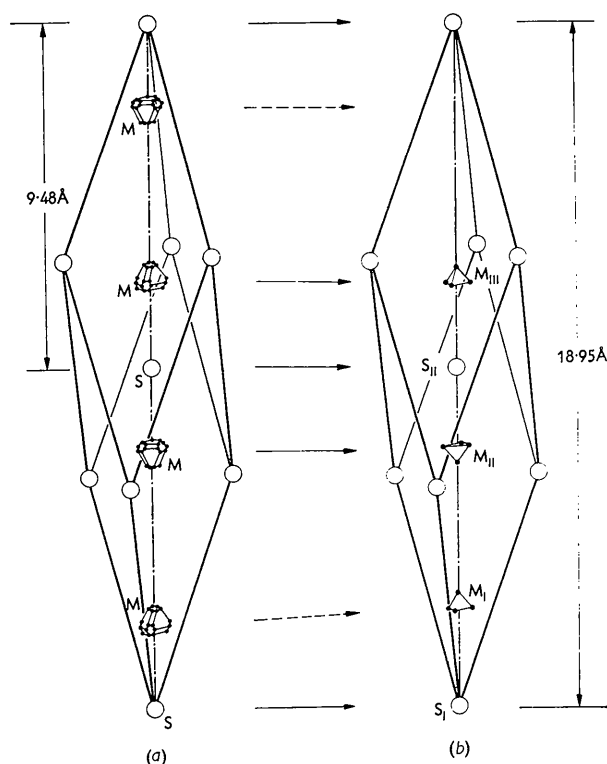


Fig. 5. Derivation of the structure of the metastable form from that of the high-temperature form.

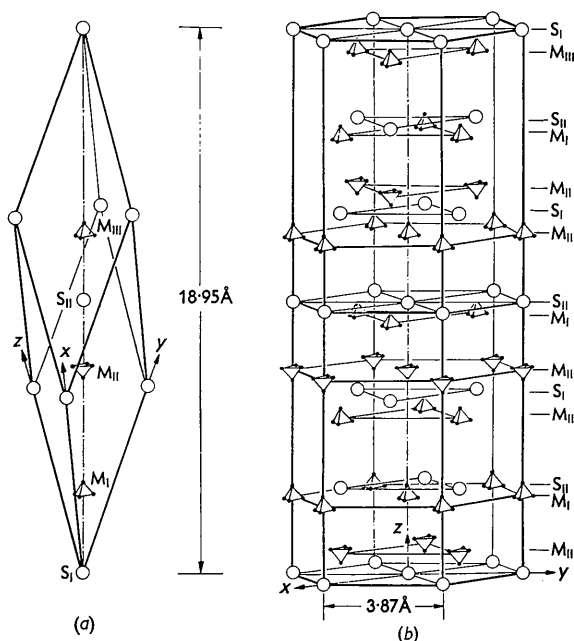


Fig. 6. Crystal structure of metastable form shown on (a) a rhombohedral cell and (b) a hexagonal cell.

show the interatomic relations. The structure is described as a layer-structure parallel to (0001). There are two kinds of sulfur layers,  $S_I$  and  $S_{II}$ , and

three kinds of metal layers,  $M_I$ ,  $M_{II}$ , and  $M_{III}$ . The  $S_I$  layers are sandwiched between the  $M_{II}$  and  $M_{III}$  layers, while the  $S_{II}$  layers only have the  $M_I$  layers on one side (Fig. 6(b)). To compensate for the lack of metal layers on the other side, unpaired  $M_I$  layers are displaced to approach the  $S_{II}$  layers.

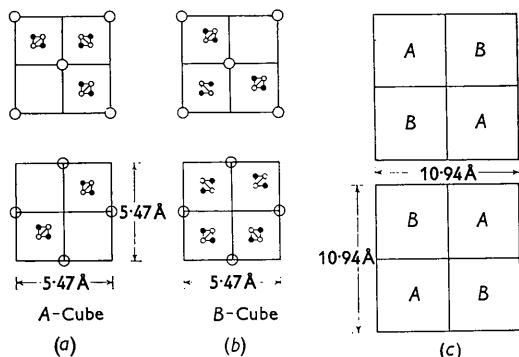


Fig. 7. The crystal structure of the metastable form based on a cubic multiple cell. The upper figures correspond to the upper halves of the cubes: (a) and (b) basic building blocks, (c) multiple cell. Large circles are S atoms, small ones are metal atoms. In (a) and (b), only the upper S atoms are shown.

The crystal structure can be also regarded as being composed of cubelets, 5.47 Å on the edge, of two different kinds, *A* and *B* (Fig. 7, (a) and (b)). The sulfur atoms, occupying the origins and the face centers of the cubelets, form eight tetrahedra. Five of them are occupied by metal atoms in the *A* cubelets, seven in the *B* cubelets. The compositions are, therefore,  $M_5S_4$  for the *A* cubelet and  $M_7S_4$  for the *B* cubelet. A cubic multiple cell with  $a=10.4$  Å contains four *A* and four *B* cubelets (Fig. 7(c)).

Table 7. Interatomic distances in the metastable form

Atom	Neighbors	Bond length
$M_I(a)$	$S_I$	2.94 Å
	$S_{II}$	2.24
$M_I(b)$	$S_I$	2.69
	$S_{II}$	{ 2.46 2.20
$M_{II}(a)$	$S_I$	2.27
	$S_{II}$	2.75
$M_{II}(b)$	$S_I$	{ 2.75 2.27
	$S_{II}$	2.27
$M_{III}(a)$	$S_I$	2.75
	$S_{II}$	2.27
$M_{III}(b)$	$S_I$	2.27
	$S_{II}$	{ 2.75 2.27

The interatomic distances (Table 7) are in good agreement with those known in copper-iron sulfides; for example: Fe-S  $2.20 \pm 0.03$  Å and Cu-S  $2.31 \pm 0.03$  Å in chalcopyrite (Pauling & Brockway, 1932), and

Fe-S 2.27 Å and Cu-S 2.31 Å in cubanite (Azaroff & Buerger, 1955). The metal atoms are coordinated to four sulfur atoms each which are at the corners of regular tetrahedra (Fig. 8). The  $M_{II}$  and  $M_{III}$  tetrahedra are at the centers of the sulfur tetrahedra and the shortest distance from any one of their corners to a sulfur atom is 2.27 Å (Fig. 8, (b) and (c)). The

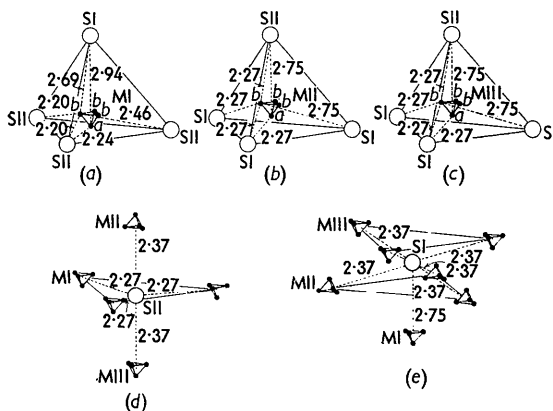


Fig. 8. Interatomic configuration of metal and sulfur atoms in the metastable form: (a) for  $M_I$ , (b) for  $M_{II}$ , (c) for  $M_{III}$ ; (d) and (e) show the distances between the sulfur atoms and the centers of the tetrahedra of metal atoms. The *z* axis points downward on all drawings except (b), where it is directed upward.

$M_I$  tetrahedra are slightly displaced from the centers of the sulfur tetrahedra (Fig. 8(a)). The smallest distances between the sulfur atoms and the  $M_I$  atoms are 2.20 Å, suggesting that the  $M_I$  positions are more likely to be occupied by Fe atoms than the other metal positions. The  $S_I$  atoms are coordinated to three  $M_{II}$  and three  $M_{III}$  at closer distances and to one  $M_I$  atom at a longer distance (Fig. 8(e)). The  $S_{II}$  atoms are coordinated to three  $M_I$  atoms at closer distances and to one  $M_{II}$  and one  $M_{III}$  atom at longer distances (Fig. 8(d)).

### Low-temperature form

The X-ray data of the low-temperature form give tetragonal symmetry with cell dimensions  $a=10.94$  Å and  $c=21.88$  Å. The space group is  $P\bar{4}2_1c (D_{2d}^4)$ . Strong and medium reflections generally have similar intensities in the metastable and low-temperature forms, indicating that the two crystal structures have a common basic structure. For the low-temperature form, however, the special extinction rules, which gave the clue to twinning in the metastable form, are no longer maintained, although the sub-cell with  $a=5.47$  Å is still present. The additional reflections of the low-temperature form fall into two groups: (a) reflections with  $h+k+l=2n$ , some of which are fairly strong, and (b) reflections with  $h+k+l=2n+1$ , which are very weak.

There are two ways of explaining the disappearance



of the special extinction rules in the low-temperature form: (1) disappearance of twinning, as the crystal symmetry changes from rhombohedral to tetragonal; or (2) lowering of the crystal symmetry from rhombohedral to monoclinic, as the twin symmetry changes from cubic to tetragonal. In the absence of any morphological or optical evidence in favor of twinning, the latter hypothesis should be justified only by the structure determination.

Although the structure of the low-temperature form was not actually determined, it seems certain that metal atoms, statistically distributed in the rhombohedral metastable form, would preferentially choose one of the sites in each position on transition. This ordering of metal atoms would be accompanied by slight adjustments of the surrounding atoms. The stoichiometric chemical formula confirmed for most natural bornite specimens suggests that the Fe atoms are ordered in the low-temperature form.

### On the transition from the high-temperature form to the metastable form

Fig. 9 shows the structural relations between the two polymorphic forms, both of which are represented as layer structures parallel to (0001). The structures of single crystals (= domain orientations) are shown for the metastable form. Both structures are built on cubic close-packing of the sulfur atoms. The statistically distributed metal atoms are represented as bands.

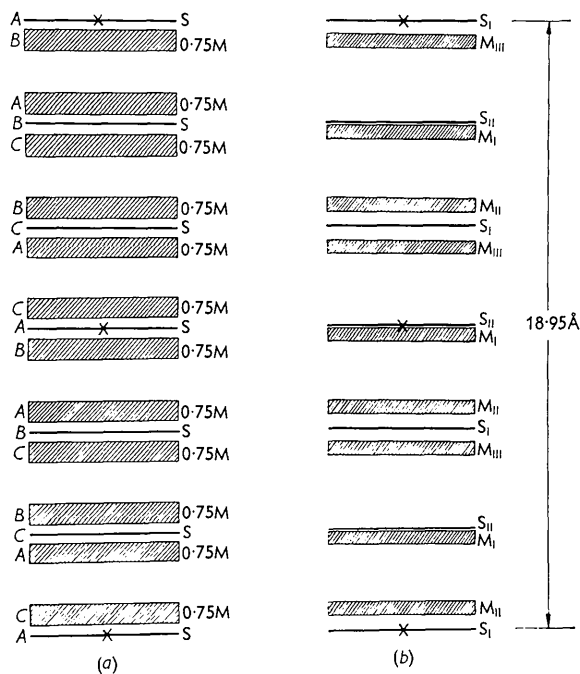


Fig. 9. Layer structures of two polymorphic forms: (a) high-temperature and (b) metastable. The positive  $z$  axis is up in (b) as in Fig. 6(b).

The arrangements of the metal-vacant layers change their orientation according to a simple twin law in the metastable form as already mentioned. Domain structures appear on transition from the high-temperature to the metastable form. This indicates that the metal-vacant layers cannot stably keep their orientation over a long distance. The diffracted X-rays from a crystal (= domain orientation) are not coherent with those from the other crystals. The domains themselves must, however, be small since the twins cannot be recognized as such by direct methods of observation. The volumes of the different domains must be nearly equal so as to simulate cubic symmetry for the specimen as a whole.

Specimens of the metastable form 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. However, they are different from usual twins in that most of the atoms build a continuous periodic structure 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 remarkably well satisfied, and twinning should be frequent, as indeed it is; it always accompanies the transition. Such slight structural rearrangements take place that the transition heat should be very small and the transition unquenchable.

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## The Structure of Coordination Compounds I. The Crystal and Molecular Structure of Azidopentamminecobalt(III) Azide

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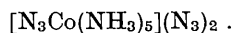
Azidopentamminecobalt(III) azide,  $[\text{N}_3\text{Co}(\text{NH}_3)_5](\text{N}_3)_2$ , forms dark red prismatic crystals, with space group *Pnam* and unit cell dimensions

$$a = 12.997 \pm 0.005, \quad b = 8.031 \pm 0.004, \quad c = 10.414 \pm 0.004 \text{ \AA}.$$

With four molecules per unit cell, the cation is required to have symmetry *m*. The azido group in the coordination sphere is asymmetric with N-N distances of 1.145 and 1.208 Å. The angle Co-N-N is 124.8°. The azide anion is symmetric and linear with N-N distances of 1.158 and 1.172 Å. The final value of the residual *R* was 7.5% for all the 1412 observed reflections.

### Introduction

A survey of the literature revealed relatively few three-dimensional structure determinations of coordination compounds. Of the three-dimensional studies reported, a smaller number were concerned with a systematic study of the bonding in coordination compounds. We have decided to investigate the structures of a series of ammine complexes of cobalt and chromium to obtain structural information on these complexes. The following represents a report of the first structural investigations in the proposed study, azidopentamminecobalt(III) azide,



The bonding of the azido group in coordination compounds has been the subject of some speculation. Linhard, Siebert & Weigel (1958) concluded that the greater shift to the red in the infrared spectra of azidopentamminecobalt salts indicated stronger metal-to-nitrogen bonding compared with the chromium complexes. Linhard & Berthold (1958) speculated that the lower impact sensitivity of azidopentamminechromium(III) salts resulted from the more polar character of the chromium-azide bond. Fujita, Nakamota & Kobayashi (1956), however, concluded from a study of the N-N stretching frequencies in the infrared that the cobalt-nitrogen bond in coordinated

azides was more ionic than the corresponding chromium-nitrogen bond. The increased ionic character was used to explain the ease of aquation of the cobalt(III) azide complex compared with the chromium(III) complexes. On the basis of infrared spectra of various azide complexes of cobalt(III), Staples & Tobe (1960) considered the azide group to be unsymmetrical and linear with the Co-N-N angle between 108 and 120°.

An X-ray crystal structure determination of azidopentamminecobalt(III) azide was undertaken to resolve the question of the bonding of the azido group in coordination compounds. The azide was chosen since it permits a comparison of both anionic and coordinated azides in the same structure determination.

### Experimental

Azidopentamminecobalt(III) azide forms dark red prismatic crystals. Rotation and Weissenberg photographs were taken with two different crystals, one with *a* and one with *b* as the rotation axis. The systematic absences observed on the Weissenberg photographs were:

$$\begin{aligned} 0kl & \text{ if } k+l=2n+1 \\ h0l & \text{ if } h=2n+1 \\ hk0 & \text{ no absences} \\ hkl & \text{ no absences} \end{aligned}$$